



HOKKAIDO UNIVERSITY

Title	Experimental Investigation of Chloride Attack in Steam-cured Concrete with Supplementary Cementitious Materials under Salt-laden Environment in Cold Region
Author(s)	Wang, Ni
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第15679号
Issue Date	2023-12-25
DOI	https://doi.org/10.14943/doctoral.k15679
Doc URL	https://hdl.handle.net/2115/93877
Type	doctoral thesis
File Information	Wang_Ni.pdf



Experimental Investigation of Chloride Attack in Steam-
cured Concrete with Supplementary Cementitious
Materials under Salt-laden Environment in Cold Region

混和材を用いて蒸気養生したコンクリートの寒冷地環境
における塩害に関する実験的研究

WANG NI

Laboratory of Environmental Material Engineering
Division of Field Engineering for the Environment
Graduate School of Engineering Hokkaido University
Sapporo, Japan
December 2023

DEDICATION

To

My beloved family

ACKNOWLEDGEMENTS

I extend my sincere appreciation to Professor Takafumi Sugiyama for his unwavering guidance throughout my academic journey. His dedication to both scholarly pursuits and the ethos of craftsmanship has profoundly influenced my academic and personal development. I firmly believe that his tremendous assistance was indispensable for the completion of my research. I extend my heartfelt gratitude to Former Assistant Professor Kazunori Shimura and Professor Michael Henry. Their guidance and suggestions have been enlightening and instrumental in shaping my research journey. I also sincerely thank to Professor Takashi Matsumoto, Associate Professor Katsufumi Hashimoto, and Associate Professor Koji Matsumoto for their insightful advice for refining the dissertation. Additionally, I would like to thank Dr. Takano (Kyowa Concrete Industry Co. Ltd.), Dr. Igarashi and Mr. Ito (Denka, Co. Ltd.), Mr. Saito (Hokuden Sogo Sekkei Co. Ltd.) and former graduated students Mr. Hou, Mr. Cahyadi, Mr. Iyoda, Mr. Saito, and Mr. Hasebe. These individuals have provided invaluable assistance during my research process, and their support and collaboration have been crucial to my research work. I would like to say thank you to my dear EME lab members for their invaluable assistance and the joy they have brought to my daily lab life.

The years of my doctoral program have been a concentrated period of exploration in my life's journey. I am grateful to every person who has crossed my path during this time, as their assistance and influence have become treasured assets that will accompany me throughout my life. Here, I want to express my appreciation to Dr. Zhang, Dr. Xu, Dr. Kim, Dr. Sun, Dr. Tonya, Dr. Merve, Mr. Kemp, and Mr. Datta. They have shown me their passion for exploring the world and living life to the fullest. I would also like to extend my gratitude to Professor Harue Ishii for her continuous guidance and mentorship. Your insights and encouragement have played a pivotal role in my personal and academic growth.

I extend my deepest appreciation to my family, my mother, Yajun Hou, and my father, Zhenwei Wang. I thank you for giving me life, unconditional love, and unwavering support in all my decisions. I love you both. I also want to thank to my cousin, Shu Wang, who has played an integral role as a guiding and supportive figure in my growth. My thanks extend to my aunt, Guijuan Wang, my uncle, Zhenyu Wang, and other family members for their continuous support. I am profoundly grateful to my partner, Philip Welin-Berger, for his constant understanding, support, and belief in me. You have been my guardian angel throughout my life journey.

I deeply appreciate my friends who have been a part of my life: Jingjing, Huiwen, my lifelong neighbor Dr. Opon, Chika, Dr. Gustavo, Mchecht, Filippo, Dr. Chan, Dr. Hamza, Yubin, Carla, Matsuda san, Dr. Tan, Dr. Cunningham, Dr. Emmanuel, Damian, Theo, Yoshida, and everyone else. Those are the most Kawaii person in my world.

I extend my appreciation to everyone who has been part of my life, and I hope for an amazing, happy and bright future for all of us.

ABSTRACT

In the cold regions of Japan, the infrastructure element has to confront the problem of getting attacked by chloride ions from severe external resource such as seawater or deicing salt, resulting in the growing risk of deterioration with service time. Opting to prolong the lifespan of partial deteriorated structures rather than completely demolishing them is a more sustainable, environmentally friendly, and cost-effective approach. Precast concrete as an alternative component can meet all the above requirements, and its versatility has attracted public attention. Steam curing is a widely employed method for producing precast concrete; however, current research on the performance and durability of precast concrete remains relatively limited. It is well-known that concrete incorporating fly ash and blast furnace slag can enhance the durability and corrosion resistance. A calcium-aluminum additive, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, effectively binds chloride ions chemically to stable solids within the concrete, improving chloride resistance. However, whether these benefits from Supplementary Cementitious Materials (SCM) still hold in steam-cured concrete has been the subject of limited study. Combining the advantages of steam curing and SCM to produce high-quality, sustainable, industrialized concrete products for replacing partially deteriorated infrastructure, such as the high-strength concrete bridge slabs in cold regions, would be an ideal prospect worth pursuing. To achieve this noble aspiration, it is essential to first understand the properties of steam cured SCM concrete. This research aims to delve into this subject by two parts of research:

The first part of the research focuses on the chloride ion resistance of steam cured SCM concrete in cold marine environments. The concrete types are categorized into four groups, along with a reference specimen (N) that solely employs ordinary Portland cement, fly ash concrete (FA) with a cement replacement rate of 15%, blast furnace slag concrete (SG) with a replacement ratio of 50% and CA concrete with 7% substitute ratio of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$. In normal-strength concrete with a binder-to-water ratio of 50%, the steam-cured specimens underwent one day of steam curing followed by 13 days of air curing (S) and steam-water curing (SW), which involved water curing for an additional 13 days following the initial day of steam curing, while the standard curing specimens (W) were subjected to 28 days of water curing. Subsequently, all the specimens were relocated to the offshore area of Hakodate, Hokkaido, for exposure to fresh seawater. Mercury Intrusion Porosimetry (MIP) experiments were conducted to analyze the changes in the pore structure of the specimens before and after exposure in steam-cured concrete. The results indicated that pore size distribution was highly correlated with the type of binder used and the curing methods. Furthermore, blast furnace slag concrete exhibited very low chloride ion diffusion coefficients (D_c) under three curing methods, while fly ash concrete tended to benefit from water curing. Notably, steam cured normal-strength CA concrete had D_c of only 0.53 compared to the reference group after one year, despite the MIP showing an increase in porosity around a pore width of 1860nm. This increase in porosity did not significantly affect its strong resistance to chloride ions. In another set of high-strength concrete all adopted

materials and curing procedures were the same but with a lower binder water ratio of 0.34 and no SW curing method. The conclusions of this part of study include that water binder ratio is the primary factor that affects chloride ion resistance. In the presence of sufficiently dense high-strength concrete, the influence of binder types and curing methods on chloride ion resistance diminishes. Therefore, the chloride ion resistance of high-strength steam-cured CA concrete is not significantly affected by the addition of CA2. It also indicates that fly ash and blast furnace slag concrete with higher cement replacement ratio are more suitable for practical SCM production of high-strength steam-cured concrete bridge slabs.

The next part focuses on the use of high-strength steam-cured concrete as a double-layer reinforced concrete bridge slab, utilizing the fly ash and blast furnace slag as SCM materials, which has been selected in the previous section. The SCM binder in this study is 20% replacement rate fly ash (FB) and 50% blast furnace slag (BB), and high early strength Portland cement is used as cement. The water-cement ratio of SCM concrete is 0.35, and the concrete with pure cement is 0.4. Additionally, specimens with the pessimism ratio of reactive andesite were prepared to investigate the corrosion resistance of high-strength steam-cured fly ash concrete under the combined damage of ASR and chloride ion attack. Each concrete series was cast with 5 specimens to account for the uncertainty of steel corrosion in high-strength steam-cured concrete. All specimens were exposed to 10% NaCl solution at a curing temperature of 40 °C. The experimental results proved that the steel bars in the SCM concrete did not corrode until the end of the three-year chloride exposure experiment and had an extremely low Dc of 0.32 cm²/year for FB concrete and 0.29 cm²/year for BB concrete. In contrast, the control specimens exhibited steel corrosion and abnormally high chloride ion diffusion coefficients due to wide longitudinal cracks caused by steel corrosion. The addition of fly ash plays a role in delaying the onset of ASR and inhibiting chloride penetration, thereby improving the corrosion resistance of concrete.

In summary, this research clarified that CA2 additive can effectively restrict chloride penetration in steam-cured concrete under cold marine exposure conditions, despite an increase in porosity within the larger pore width after one year. In addition, high-strength steam-cured concretes with fly ash demonstrated better resistance against the corrosion of steel bars even under combined chloride attack and ASR risk. Moreover, the half-cell potential method can effectively assess the corrosion condition of steel bars within the thick concrete cover of high-strength steam cured concrete, in which the disruption of daily traffic services could be avoided.

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION.....	1
1.1 General Background	1
1.2 Steam-cured Supplementary Cementitious Materials (SCMs) Concrete	3
1.3 Combined Damage of ASR and Chloride Attack in Concrete	4
1.3.1 Chloride penetration in concrete	4
1.3.2 Concrete elements in Marine environment	4
1.3.3 Chloride-related corrosion in reinforced concrete subjecting to deicing salts	6
1.3.4 Alkali-silica reaction (ASR)	7
1.3.5 Chloride ions binding in concrete	8
1.4 Corrosion Monitoring of Steel Bars by Half-cell Potential Method..	12
1.5 Research Objectives.....	12
1.6 Thesis Structure	14

CHAPTER 2

CHLORIDE RESISTANCE OF STEAM-CURED SCMS CONCRETE IN COLD-REGION MARINE ENVIRONMENT	16
2.1 Introduction.....	16
2.2 Research Scope	16
2.3 Materials and Experiments	17
2.3.1 Mix proportion.....	17
2.3.2 Specimens preparation	18
2.3.3 Methodology	21
2.4 Compressive Strength of Steam-cured SCMs Concrete	23
2.4.1 Compressive strength of normal-strength SCMs concretes.....	23
2.4.2 Influence of steam curing on the compressive strength development of normal-strength SCMs concrete	25
2.4.3 Compressive strength of high-strength SCMs concretes.....	28
2.4.4 Influence of steam curing on the compressive strength development of high-strength SCMs concrete.....	29

2.4.5 Influence of water binder ratio (W/B) on the compressive strength developing of SCMs concrete in various curing methods	30
2.5 Mercury Intrusion Porosimetry Experiment (MIP)	32
2.5.1 Mercury intrusion in normal-strength SCMs concrete before seawater exposure	32
2.5.2 Mercury intrusion in normal-strength SCMs concrete after seawater exposure for one year	42
2.6 Chloride Penetration in Steam-cured SCMs Concrete.....	49
2.6.1 Chloride resistance of normal-strength SCMs concrete exposed to seawater for one year	49
2.6.2 Effect of binder types and curing methods on chloride penetration in normal-strength steam-cured SCM concrete in marine environment	57
2.6.3 Chloride penetration in high-strength SCMs concrete exposed to seawater for one year	62
2.7 Summary	65

CHAPTER 3

CORROSION EVALUATION OF DOUBLE LAYERS STEEL REINFORCEMENTS EMBEDDED IN HIGH-EARLY- STRENGTH STEAM-CURED SCMS CONCRETE SLAB SUBJECTED TO CHLORIDE PENETRATION.....

3.1 Introduction.....	66
3.2 Research Scope	66
3.3 Materials and Experiments	67
3.3.1 Mix proportion.....	67
3.3.2 Specimens preparation and curing methods	68
3.3.3 Electrochemical technique for corrosion diagnosis	71
3.4 Properties of High-early-strength Steam-cured SCMs Concrete.....	73
3.4.1 Compressive strength.....	73
3.4.2 Freezing and thawing test	73
3.5 Accelerated Expansion Test of Concrete Incorporating Active Alkali Andesite	74
3.6 Corrosion Evaluation via Electrochemical Technique	76
3.6.1 Corrosion diagnosis of double layer rebars using half-cell potential method.....	76
3.6.2 Six combinations of half-cell potential measurements	79
3.6.3 Efficient corrosion diagnosis through JB potential measurement	80
3.6.4 Corrosion resistance of high-early-strength steam-cured SCMs concrete	81

3.7 Appearance of Concretes and Steel Bars after Long-term Chloride Exposure Experiment.....	87
3.7.1 Specimens of H, FB, and BB concrete	87
3.7.2 Specimens of HA and FBA concrete	91
3.8 Chloride Resistance of High-early-strength Steam-cured SCMs Concrete	94
3.8.1 Chloride penetration in high-early-strength steam-cured SCMs concrete	95
3.8.2 Effect of fly ash on steel corrosion resistance of high-early-strength steam-cured concrete under combined damage of ASR and chloride attack	98
3.9 Summary	100

CHAPTER 4

CONCLUSIONS AND FUTURE WORKS	101
4.1 Conclusions.....	101
4.2 Future Works	102
REFERENCES	103
APPENDIX A.....	111
APPENDIX B	115
APPENDIX C	122
APPENDIX D.....	130
APPENDIX E	135
APPENDIX F	137

LIST OF TABLES

Table 1	Mix proportions of 24 series and 50 series
Table 2	Experiments and specimens for 24 series and 50 series
Table 3	Surface water permeability coefficient of 24 series concrete
Table 4	Critical pore size in 24 series concrete
Table 5	Increased/Decreased porosity in three pore size intervals after one year seawater exposure
Table 6	Apparent chloride diffusion coefficient (D_c) of 24 series concrete
Table 7	Depth of high-concentration chloride region and overall chloride diffusion front in EPMA images of 24 series concrete
Table 8	D_c ratio of 24SCM series compared to the respective N series under three curing methods after one-year seawater exposure
Table 9	Apparent chloride diffusion coefficient (D_c) of 50 series concrete
Table 10	Mix proportions of high-early-strength steam-cured SCMs concrete
Table 11	Experiments and specimens for high-early-strength steam-cured SCMs concrete
Table 12	Properties of high-early-strength steam-cured SCM concrete
Table 13	Estimated corrosion initiation (T_i) via the half-cell potential method
Table 14	Durations for Corrosion meter measurement in each series
Table 15	Corrosion current (I_{corr}) and concrete cover resistivity (R_{es}) measurements via Corrosion meter
Table 16	Verified corrosion condition of rebars in observation experiment
Table 17	Total chloride ion concentration at depths around the upper and down bar in five types of concrete
Table 18	Apparent chloride diffusion coefficients (D_c) and chloride surface concentrations (C_0) in central part and side part

LIST OF FIGURES

Figure 1.1	Schematic illustration of a steel corrosion cell in concrete
Figure 1.2	ASR damage in concrete
Figure 1.3	Outline of the dissertation
Figure 2.1	Steam curing set and the temperature in concrete
Figure 2.2	Processes of three curing methods before seawater exposure
Figure 2.3	Seawater exposure site in Hakodate, Japan
Figure 2.4	Seawater temperature variation from November 2018 to December 2019
Figure 2.5	Sampling processes for chloride content measurement in concrete
Figure 2.6	Compressive strength of 24 series under three curing methods over one year
Figure 2.7	Compressive strength development of 24SCM series concrete under three curing methods over one year
Figure 2.8	Compressive strength of 50 series concrete under standard curing and steam-air curing over one year
Figure 2.9	Compressive strength development of 50SCM series concrete under standard curing and steam-air curing over one year
Figure 2.10	Cumulative intrusion curves of four types of 24 series specimens under three curing methods before seawater exposure
Figure 2.11	Pore size distribution curves of four types of 24 series specimens under three curing methods before seawater exposure
Figure 2.12	Distributed porosity in three pore size intervals of four types of 24 series specimens under three curing methods
Figure 2.13	Self-comparison of porosity in three pore size intervals of four types of 24 series specimens under three curing methods
Figure 2.14	Pore structure of four types of 24S series specimens after one-year seawater exposure (24S-1Y)
Figure 2.15	Evolution of pore size distribution of 24 series under three curing methods during one-year seawater exposure
Figure 2.16	EPMA images of the 24W-1Y series and the 24S-1Y series
Figure 2.17	Chloride profiles of 24 series under three curing methods for one-year seawater exposure
Figure 2.18	Relationship of Dc and depressurization porosity of 24S-1Y series
Figure 2.19	Chloride profiles of 50 series under standard curing and steam-air curing over one year
Figure 3.1	Temperature processes of steam curing for high-early-strength steam-cured SCM concrete
Figure 3.2	Scheme illustration of double layers reinforcements concrete with NaCl solution pool
Figure 3.3	Temperature changes of Freezing and Thawing cycles in 24 hours

Figure 3.4	Specimen curing processes for chloride penetration experiment
Figure 3.5	Six combinations for half-cell potential measurements
Figure 3.6	Schematic diagram of Corrosion meter
Figure 3.7	Results of accelerated length change experiment
Figure 3.8	Active andesite and surrounding composition of concrete
Figure 3.9	Half-cell potential results of five types of concrete
Figure 3.10	Scatter plot distribution of JB-UT and JT-UT for five concrete types
Figure 3.11	Appearances of five types of concrete before/on the split date, and rebars on the split date
Figure 3.12	ASR cracks on HA3 concrete surface and corroded steel bars at 490 days
Figure 3.13	Sampling locations of central part and side part for chloride content measurement
Figure 3.14	Chloride profiles of five concrete types at central part and side part

CHAPTER 1

INTRODUCTION

1.1 General Background

The degradation of reinforced concrete structures due to chloride-induced corrosion is a prevalent durability issue worldwide, particularly in environments exposed to salt resource, such as seawater and de-icing salt conditions (Glasser et al., 2008; Ragab et al., 2016). The concrete cover serves as a protective barrier for the embedded reinforcements, primarily responsible for preventing direct contact of harmful ions from exposure environment with the steel reinforcement and maintaining a stable environment for the passivation layer of the steel bar (Qu et al., 2021; Shi et al., 2012). Consequently, the quality of the concrete layer undoubtedly contributes to decreasing the risk of steel corrosion. For reinforced concrete structures exposed to corrosive environments or subjected to prolonged service life, localized deterioration is inevitable. However, compared to the collapse of the entire structure, the sustainable approach lies in the replacement of deteriorated sections with sound concrete elements. In those circumstances, the replaceable concrete elements can meet the maintenance needs, providing a controllable quality and benefits the purpose of reducing labor. Therefore, precast concrete has drawn more and more attention because it can utilize as a substitute element for partial corroded reinforced concrete sections without destroying the integrity of the building. Steam curing is a commonly employed technique for precast concrete, and steam-cured concrete specimens have demonstrated their outstanding commercial value. However, the investigation of chloride resistance and corrosion resistance in steam-cured reinforced concrete is far less than in standard-cured concrete, especially with respect to concrete incorporating supplementary cementitious materials.

Supplementary cementitious materials (SCMs) have given their superior performance in standard cured concrete in numerous instances and hold promise to decrease CO₂ emissions (Poon et al., 2000; Cheewaket et al., 2010; Kayali et al., 2012; Ramezaniapour & Malhotra, 1995). Fly ash and blast furnace slag are the most widely used SCMs in the concrete industry. The pozzolanic reaction and latent hydraulic reaction contribute to provide long-term strength and a compact pore structure. Moreover, the high aluminum phase increases the chloride binding capacity, mitigating the risk of the steel corrosion caused by chloride diffusion. Additionally, in concrete containing silica-reactive aggregates, alkali substances in the pore solution preferentially react with the fine particles of SCMs, thus retarding the onset and extent of Alkali-Silica Reaction (ASR) damage (Ichikawa, 2009, Hong & Glasser, 1999). Therefore, their potential to enhance the durability of steam-cured concrete is anticipated. Considering the chloride resistance of concrete, a calcium-aluminate additive, CaO·2Al₂O₃ (CA2), has garnered attention for its capacity to bind chloride ions. The binding mechanism involves CA2 reacting with calcium hydroxide (CH) to produce hydrocalumite (HC), whose hydration products additionally contribute to the densification of concrete. Subsequently, hydrocalumite binds chloride ions to form

Friedel's salt in concrete solid, thereby enhancing the chloride resistance of the concrete cover. (Tabara et al., 2010 & 2013, Miyazaki et al., 2021). CA2, the second component in Calcium Aluminate Cement (CAC), has received limited attention primarily because of its low hydraulic properties, which are associated with its low calcium aluminate ratio. Conversely, its high aluminate phase content and extended hydration are precisely valuable attributes for providing concrete with long-term resistance to chloride penetration. Moreover, another appealing aspect of CA2 as an SCM is that its substitution rate of less than 10% does not require the additional preparation of storage facilities during the concrete production process. There is considerable research space in the study on chloride resistance of concrete incorporating CA2, especially in the relatively unexplored field of its application in steam-cured concrete. Consequently, further research is needed to investigate the various properties of SCMs in the context of steam curing.

Reinforced concrete bridges in Hokkaido consistently face heavy snowfall-winters and the demands of de-icing salts, which may elevate the risk of steel corrosion to pose a challenge to their long-term serviceability. In cases where the aggregates of concrete used contain silica-reactive materials, the alkali metal cations in de-icing salts have the potential to initiate ASR, leading to a more complex environmental condition within the concrete. Furthermore, the utilization of SCMs is one efficient means to enhance the durability of concrete structures. However, in the absence of a complete understanding of the performance of SCM concrete in steam curing conditions, there is even less research available concerning the interplay of ASR threats and chloride attacks and their cross-influence on the corrosion of steel bars in steam-cured concrete (Wang & Sugiyama, 2022). On the other hand, the corrosion of steel bars embedded in high-strength concrete slabs is challenging to detect synchronously and precisely due to the thick concrete cover. When corrosion traces appear on the concrete surface usually means the damage to rebars has entered a relatively late stage of propagation (Angst et al., 2009). This poses a threat to both personal safety and economic losses. Furthermore, the maintenance of bridges necessitates a substantial investment of time and human resources, this presents a significant challenge to Japan's society, particularly in the current context of a shortage of skilled labor. Therefore, it is urgent to find an effective and practical method for diagnosing steel corrosion that provides accurate detection of corrosion while being operationally convenient, ideally allowing for detection without disrupting traffic usage. A non-destructive detection, half-cell potential method has entered the field of vision, which can fulfill the aforementioned requirements for detecting corrosion in concrete-embedded steel reinforcement (Elsener et al., 2003; Andrade & Alonso, 2004). Nevertheless, it remains to verify the effectiveness that this electrochemical method diagnoses the corrosion of steel bars in high-strength steam-cured SCMs concrete slabs with thick concrete layers (Wang et al. 2021). Consequently, further research is necessary to enhance our understanding of the chloride-related corrosion resistance of steam-cured SCMs concrete and to explore corrosion diagnosis methods for the embedded steel reinforcement within a thick concrete cover.

1.2 Steam-cured Supplementary Cementitious Materials (SCMs) Concrete

The service life of infrastructure extends the possibility of deterioration increases. In Japan, 28% of infrastructure constructions have reached a service life of over 50 years in 2021. In these cases, the concrete elements are usually accompanied by localized failure rather than structural integrity collapse. Besides, concrete elements can apply quickly to post-disaster reconstruction projects, which are appreciable for areas prone to natural disasters. Precast concrete products enter the engineering views, which can replace damaged parts of the structure and compromise the integrity of the building. Moreover, precast concrete elements can relieve the limitation of building fields in the low-temperature region, shorten the production duration, increase economic benefits, and alleviate the problem of labor shortage in Japan. Steam curing is a common method for casting precast concrete. The concrete elements suffer elevated temperature and sufficient humidity in the initial curing stage to attain high early strength and a higher hydration degree achieving 80% on the first curing day (Hanif et al., 2017; Zeyad et al., 2022). However, steam-cured concrete still gives some arguments about the later strength, and rough inner structure related to higher permeability, thermal damage, and adverse effects on the concrete surface (Kjellsen et al., 1991; Escalante-Garcia & Sharp, 1998; Zain & Radin, 2000 and 2001; Zeyad et al., 2022, Yang et al., 2014). Those evidence present that steam curing has two sides of influence on the nucleation reaction of cement particles in the curing processes.

As well known, supplementary cementitious materials like fly ash and blast furnace slag brought improvements to concrete properties on aspects of permeability, durability, and ultimate compressive strength because of the filler effect and hydrated reaction in the long term (Lawrence et al., 2003; Poon et al., 1999; Nedunuri et al., 2020). However, their lower hydration reactivity at an early age leads to a lower early strength which is a common concern for SCMs concrete. The high-temperature treatment with sufficient humidity could be an effective curing method to stimulate the pozzolan materials and latent hydraulic materials to gain a high early strength to meet the concrete industry's desire (Escalante-Garcia & Sharp, 1998; Namluk & Nawa, 2011; Yazici et al., 2010). The steam cured SCMs concrete could refine the pore structure but reported a higher overall porosity in initial period. The promotion degree of pozzolanic reaction in fly ash concrete and the later development of concrete properties largely depend on the steam curing temperature and curing process (Gonzalez-Corominas et al., 2016). Furthermore, the CA2 additive is effective in reducing chloride penetration in concrete, but the behavior of CA steam-cured concrete owns minimal research. The "crossover effect" on compressive strength, a similar issue with steam-cured normal concrete, also presents in the steam-cured SCMs concretes, and it is strongly related to the Water and Binder ratio, the nature of SCMs, and the curing condition (Çakır Ö & Aköz, 2008; Castellano et al., 2016). For multiple influences of factors on the hydration process in the long-term, the effect of steam curing on the pozzolanic reaction and hydraulic reactions of SCMs needs further study.

1.3 Combined Damage of ASR and Chloride Attack in Concrete

1.3.1 Chloride penetration in concrete

The branch offices of the Ministry of Land, Infrastructure and Transport (MLIT) of Japan stated that chloride-induced corrosion of steel reinforcement is a primary issue in coastal areas and regions where de-icing salts are used on roads during the winter in Japan. Chloride attacks in concrete often accompany other forms of damage, such as freeze-thaw cycles (FTC) and alkali-silica reaction (ASR), accelerating the overall concrete integrity collapse (Tanaka et. al., 2017). The presence of abundant salts and alkali metal ions in marine environments and de-icing salts can lead to salt scaling and exacerbate ASR reactions, resulting in more surface and internal concrete cracking, which facilitates the penetration of chloride ions to greater depths. Salt-attack corrosion incurs substantial maintenance expenses for prestressed reinforced concrete bridges in Japan, and mitigating this by early prevention or ensuring longer durability of replaced bridge components would alleviate both safety and economic pressures (Kimura et al., 2010). Adequate quality of concrete cover exerts a protective role of a physical barrier between the aggressive environment and the steel bars, and the concrete pore solution provides a stable environment for the remaining passivation film of steel bars. However, ions ingress in concrete is inevitable during the service. The following content introduces the diffusion of multiple ions in concrete during exposure to seawater, as well as the role of deicing salt in initiating corrosion in reinforced concrete.

1.3.2 Concrete elements in Marine environment

An ample number of dissolved ions in the ocean, where the concrete structure can suffer simultaneous attacks from multiple ions through physical and chemical. Some typical concentrations of the anions and cations in seawater, a sufficient amount of sodium and chloride ions present at about 11000 mg/l and 20000 mg/l. Sulfate and magnesium ions also numerously existed around 2700 mg/l and 1400 mg/l, and calcium and potassium ions around 400 mg/l and 380 mg/l. Those soluble ions ingress into the depth of concrete through various driven forces from the saturation of concrete, the external environment, and spatial variability (Otieno et al., 2016). In this study, diffusion is the predominant introduction present on the content.

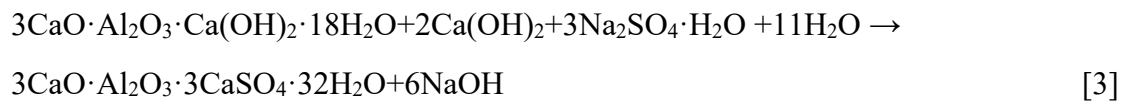
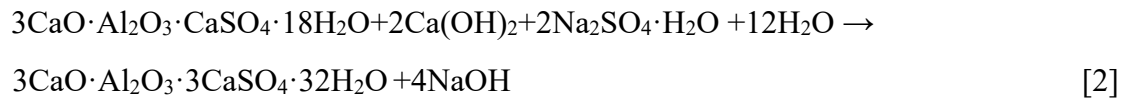
It well knows that a certain level of chloride ions could lead to steel corrosion, so its penetration in concrete received additional attention from extensive studies (Cheewaket et al., 2010; Qu et al., 2021; Luping, 2003). Generally, the trails of chloride diffusion offer a chloride profile with a concentration gradient decreasing from outward to inward of concrete. The solution of Fick's second law governs the predict the diffusion coefficient in a non-steady state (Equation [1]).

$$C_x = C_0 \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{t \cdot D_c}} \right) \right) \quad [1]$$

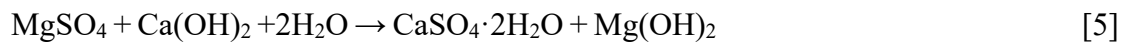
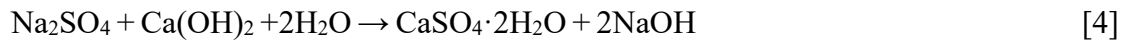
where C_x is the chloride concentration in depth concrete (mol/l), C_0 is the chloride

concentration in the concrete surface (mol/l), D_c is the diffusion coefficient (cm^2/year), t and x present time (year) and depth (cm).

In addition to the chloride attacks, the sufficient concentration of sulfate ions in seawater may also cause concrete elements to be problematic. Generally, sulfate attacks divide into two types (Dyer, 2014). The first type is because the sulfate ions attack alumina-bearing phases of hydrated cement preferentially to form ettringite accompanying cations associated with sodium, potassium, or calcium. Normally, the alumina-containing hydrates are generated by the hydrated C_3A particles in the Portland cement. The formation of hydrates depends on the proportion of C_3A in the cement mass. Monosulfate ($\text{C}_3\text{A}\cdot\text{CS}\cdot\text{H}_{18}$) is the primary product when the C_3A content is in the range of 5% to 8%, while the percentage of C_3A exceeds 8%, $\text{C}_3\text{A}\cdot\text{CH}\cdot\text{H}_{18}$ as an extra product present in the paste. The reaction processes of sulfate attacks to calcium aluminate hydrates show in Equations [2] and [3].



When the cement system runs out of the calcium aluminate phase, another result of ion-exchange reactions of sulfate attacks is to convert the concrete constituent to gypsum, shown in Equation [4]. Particularly, in the case of a magnesium sulfate attack, MgSO_4 reacts with CH to generate gypsum silica gel, and insoluble magnesium hydroxide could reduce the alkalinity content in the pore solution (Equation [5]). Furthermore, the formation products of silica gel can further react with $\text{Mg}(\text{OH})_2$ to form a soft white material giving an approximate composition of $4\text{MgO}\cdot\text{SiO}_2\cdot 8.5\text{H}_2\text{O}$ (Cole & Hueber, 1957). Consequently, magnesium sulfate attacks cause the loss of strength and stiffness of concrete, which is more severe than the formation of expansive ettringite to the integrity of the concrete. Sulfate attack ultimately leads to the deterioration of calcium oxide (CH) and results in the decalcification of the CSH structure. The degradation processes of sulfate attack are exhibited in Equations [4-6].



Although the formation of ettringite is preferential from sulfate attacks, the fact is that the marine construction usually happens damage due to the mass loss of solid constituents and the erosion (Metha, 2004). The interaction among multiple ions with concrete component is significant than single deterioration affects the behavior of concrete elements in seawater. Sugiyama (2008) had provided a model for the chemical equilibrium of the Ca leaching from the dissolve calcium oxide and CSH decalcification combined with the sodium chloride diffusion and concluded that the permeability of concrete in long-term, which was significantly affected by the multiple ions coexisting.

In addition to the interaction between multiple ions, the cement paste pore wall is generally negatively charged and attracts cations in the pore solution like Ca^{2+} , Na^+ , and K^+ but the restriction distance is only about 4nm (Friedmann et al., 2008). On the other hand, the role of ions is not immutable, for instance, the brucite from magnesium sulphate attacks forms a dense layer in the concrete surface with time. Additionally, the composition of seawater and temperature also affect the reactions of ions with concrete solid on the way of stabilization (Costa & Appleton, 1999).

1.3.3 Chloride-related corrosion in reinforced concrete subjecting to deicing salts

In cold regions, snow-covered reinforced concrete bridges widely spray deicing salts to ensure proper transportation services. Chloride-related corrosion is the greatest concern of steel corrosion, in which chloride ions accumulate to a certain level around the interface of paste and steel bars to threaten the passivation of reinforcement under risk. At present, the mechanism of chloride-related corrosion is not completely clear. However, it is wide agreement that the chloride complexes formed by chloride ions with iron from the passive film to form typical pit corrosion follow the manner of a depassivated process like Equation [7] (Hoar & Jacob, 1967). One corrosion model is that a threshold content of chloride ions with moisture may destroy the passive film after forming hydrochloric acid and acid hydrolysis of ferrous ions due to the reducibility of ferrous ions. A simplified schematic illustration of a steel corrosion cell in the concrete presents in Figure 1.1, which includes chloride ions dissolving the passivated film and the electrochemical corrosion of exposed iron follows up.



In a galvanic corrosion cell on a steel bar, the depassivated part of the steel bar possess a relatively high potential, where the exposed pure iron takes the form of ionization and plays the anodic role (Equation [8]). The passivated film is more stable to be the cathode, the surface area exposed to oxygen and humidity that undergoes a reduction reaction (Equation [9]). The pore solution between the ITZ of cement paste and reinforcement acts electrolyte, where chloride ions can repeatedly participate in destroying the passivated film. Naked iron does not stand the activation, but the spot of steel corrosion usually occurs in the position with the deficient crystal structure of iron (Dyer, 2014).



Mobilized ferrite ions undergo various subsequent oxidation reactions to form a mixture of ferrite hydroxides with the maximum expansive volume up to 6 times. Not like the rate of steel corrosion is limited by the concentration of accessible oxygen and solution, the expansion forces and volume change of corrosion products are uncontrollable. When corrosion cracks are present on the concrete surface implies a vast number of aggressive ions directly access to steel bars to exacerbate the deterioration of reinforced concrete structure, as shown in Figure 1.1. Therefore, the

repair maintenance must be secluded promptly. Furthermore, a concept of the critical chloride threshold level (CTL) has been built for representing the chloride threshold in concrete that may cause the protective film to be depressive. However, based on the data deemed by studies, it seems that CTL is hard to take into account in a realistic reference because of the diversity of the internal environment of concrete (Angst et al., 2009; Alonso & Sanchez, 2009). Hence, a common chloride tolerance for corrosion is that the chloride content is less than 0.05% of concrete mass. In addition to the factor of chloride ions, the concentration of dissolved oxygen, saturation, the Cl/OH ratio, environmental temperature, and the resistivity of concrete all play a role in influencing the electrochemical corrosion process within concrete (Alonso et al., 2000).

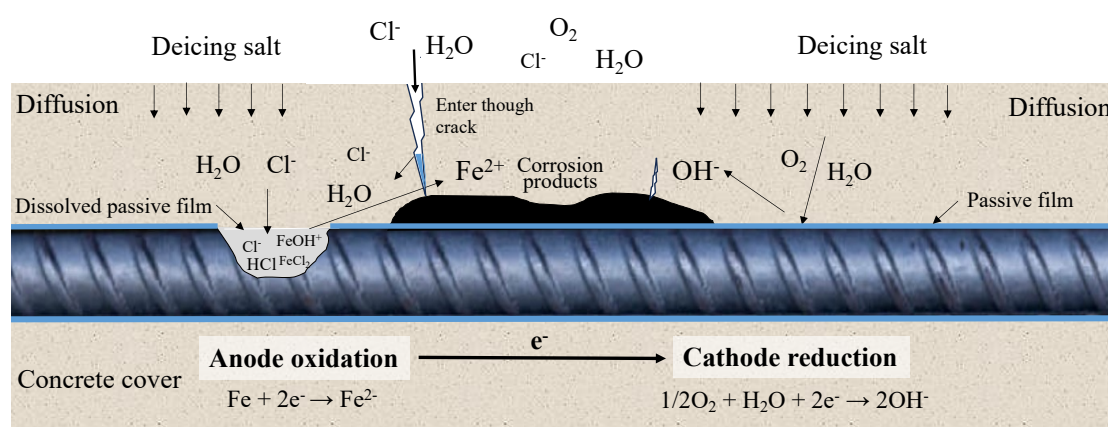


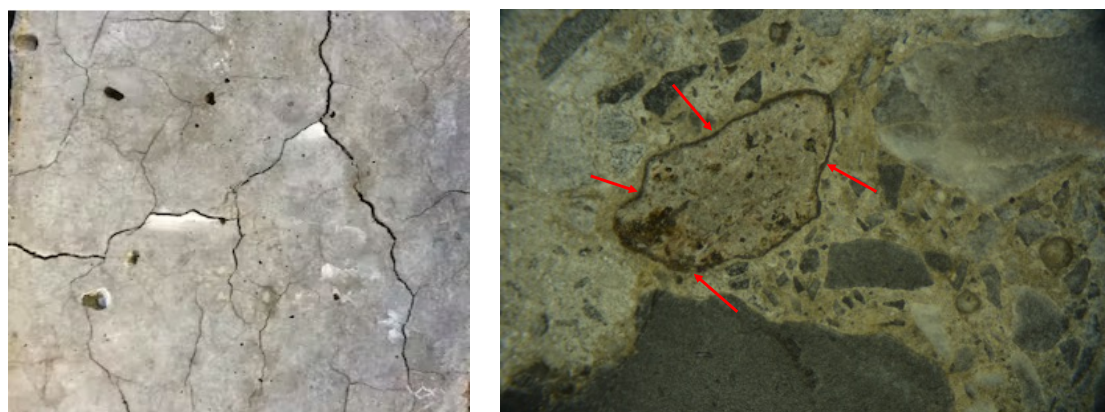
Figure 1.1 Schematic illustration of a steel corrosion cell in concrete

1.3.4 Alkali-silica reaction (ASR)

Alkali-silica reaction (ASR) is another main factor causing the deterioration of prestressed reinforced concrete bridges in Japan. It is a chemical reaction occurring between the highly alkaline pore solution in the cement paste and aggregates with sufficient reactive silica content. During ASR process, ASR-gel accumulates in reaction rim and generates expansive pressure, resulting in cracking of the aggregate and the surrounding paste (Glasser, 1991; Fournier & Bérubé, 2000; Ichikawa, 2009). Figure 1.2 shows (a) the cracks on the concrete surface subjected to ASR and (b) the reaction rim formed when the ASR occurs in the concrete exposed to a high sodium chloride environment, respectively. Although, the damage mechanism of the ASR gel to concrete is still an argument, it is acceptable view that a salt-rich environment could accelerate to initiation of the ASR, and the generating ASR cracks promote the penetration of the salt solution into the concrete, raising the corrosion of steel bars (Ichikawa & Miura, 2007; Bangert et al., 2004; Heisig et al., 2016; Chatterji et al., 1987). In addition, it is pointed out that sodium chloride solution in deicing salt and seawater can accelerate the ASR without consuming the OH⁻ in early stage due to the presence of sodium and chloride ions (Kawamura & Ichise, 1990). If concrete is subjected to combined damage from ASR and chloride attack, the cross-influence of these factors presents significant challenges to the durability of reinforced concrete and cannot be overlooked. On the other hand, some research report suggesting that ASR acts a role on protecting steel from corrosion by covering the steel surface with ASR gel, and the

harmless expansion can lead to the compaction of concrete (Ueda et al., 2014; Habuchi et al., 2004). In other words, the impact of ASR on chloride-related corrosion largely depends on the degree of ASR development, implying that corrosion resistance receives the influence from ASR that may vary within different locations of the same specimen.

Concrete incorporating fly ash and blast furnace slag, pozzolanic reaction and latent hydraulic reaction, delay ASR onset and slow down the expansion by preferentially reacting with alkalis (Ichikawa, 2009; Hong & Glasser, 1999). SCMs also contribute to reducing the formation of ASR-induced cracks by obstructing the ingress of other aggressive ions into the concrete. The hydration products of SCMs filling around active aggregate, thereby hindering mass transfer to form the reaction rims (Kawabata & Yamada, 2017; Cheewaket et al., 2010). Furthermore, SCMs that bind Cl^- ions also exert a drag lag effect on accompanying alkali metal cations. Hence, concrete incorporating fly ash is suitable for reducing the combined damage of chloride attack and ASR. Whether it delivers the same remarkable performance in high-strength steam-cured concrete bridge slabs, which requires further investigation.



(a) ASR cracks

(b) Reaction rim

Figure 1.2 ASR damage in concrete (a) ASR cracks on the concrete surface, (b) the reaction rim around active andesite aggregate (Pictures from Wang & Sugiyama, 2022)

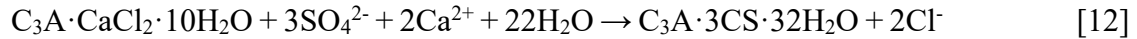
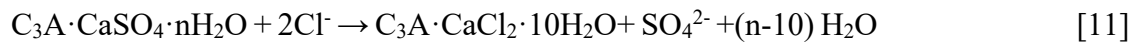
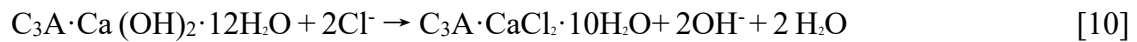
1.3.5 Chloride ions binding in concrete

Now that the role of free chloride ions in causing steel corrosion has been understood, chloride binding capacity becomes a significant factor in suppressing chloride transport in the concrete system. Generally, the chloride ions binding in the solid phase of concrete includes physical and chemical ways. However, not only are the free ions responsible for the corrosion initiation, but the bound chloride may also release chloride ions into the pore solution under specific conditions. Thus, this research uses total chloride instead of free chloride to evaluate the corrosion risk of steel bars.

1) Chemical binding of chloride ions in cementitious matrix

It is widely known that a high content of calcium aluminate phase, C_3A and C_4AF , in the cement intense the chemical chloride binding capacity of concrete via forming Kuzel's salt ($\text{C}_3\text{A} \cdot 0.5\text{CaCl}_2 \cdot 0.5\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$), Friedel's salt ($\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) and

Friedel's salt analog (Glass & Buenfeld, 2000; Khan et al., 2017). However, C₃A and C₄AF had been consumed in the initial hydration. Therefore, in hydrated cementitious system, chloride binding capacity mainly attributes to the chemisorption of calcium aluminate-bearing monosulfate (AFm) to form a stable structure like Friedel's salt and Kuzel's salt (Glasser1999, Shi 2017; Suryavanshi & Swamy, 1996(1)). AFm family, the hydration products of C₃A, consists of a group of similar members of hydrated calcium aluminates that have a hydrocalumite-like structure based on $x\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ with monosulfate type including C₃A·CaSO₄·nH₂O (SO₄-AFm), C₃A·Ca(OH)₂·nH₂O (OH-AFm), C₃A·CaCO₃·10H₂O (CO₃-AFm), C₂A·SiO₂·8H₂O (SiO₂-AFm), and 4CaO·0.9Al₂O₃·1.1SiO₂·0.5Na₂O·16H₂O (NaOH-AFm), so Friedel's salt can also be noted as Cl-AFm. Among the various AFm phase under certain circumstances, SO₄-AFm, OH-AFm, CO₃-AFm, and Cl-AFm are interconvertible because those AFm phases are thermodynamically metastable (Glasser et al., 1999). Common anion exchange of OH-AFm, chloride ions replace the hydroxyl to form the end member shown in Equation [10] (Suryavanshi et al., 1996(2)). The process of chloride ion bound with SO₄-AFm phase presents in Equation [11]. However, Friedel's salt may encounter forming ettringite due to the sulfate ion concentration in the ocean (Equation [12]).



On the other hand, the Si within the CSH phases can undergo partial substitution by Al to form calcium aluminum silicate hydrates (CASH), which stands as the most prominent hydrated product in cementitious systems, showcasing its capacity for chemisorption to bind chloride within the diffuse layers (Beaudoin et al., 1990; Thomas, 2011; Fernández & Ruiz, 2016). CASH shows on all original or blended Portland concrete, particularly in concretes that incorporates fly ash and blast furnace slag due to their high aluminum content. In contrast, in SCMs-based concrete, where the use of SCMs reduces the calcium content because of cement dosage reduction, a lower Calcium-to-Silica (C/S) ratio in the hydrated products may result in decreased chloride absorption (Zibara, 2001; L'Hôpital et al., 2016).

2) Physical binding of chloride ions in cementitious matrix

Calcium silicate hydrates (CSH) is mainly responsible for the physical absorption of chloride ions into the solid phase (Diamond, 1986). Even though most of the physical chloride binding is reversible, CSH has taken into account the contribution of the absorption of chloride ions because it has a large surface and an amount of occupation in the hydration products. The mechanism of this interaction might be caused by the positive potential of the surface of CSH, where the calcium-silicon ratio affects the physical binding stability (Zibara et al., 2016; L'Hôpital 2016). The electrical double layer (EDL theory) is also adopted to explain the binding capacity of CSH (Luping &

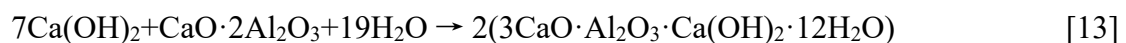
Nilsson, 1993). Nguyen and Amiri (2014) schemed a model of the EDL and the ion distribution. Simplifying the theory of EDL in the absorption aspect, the surface of cement hydration products normally presents a negative charge because of the silanol sites, which capture cation ions like Ca^{2+} , K^{+} and Na^{+} in the alkaline pore solution (Friedmann & Amiri, 2008). These cation ions form a compact layer (Stern layer) to attract anion ions such as Cl^{-} and OH^{-} in the diffuse layer of the solution to reach potential neutrality. It implies that the potential difference between the Stern layer and the diffuse layer (so-called Zeta potential) determines the absorb function of CSH to chloride ions.

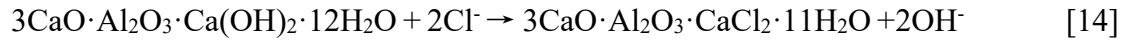
3) Chloride ions binding in conventional SCMs concrete

Fly ash and blast-furnace slag concrete under adequate proportion significantly enhance chloride resistance primarily through physical way and secondary chemical binding (Dhir et al., 1996 & 1997, Lawrence et al., 2003; Poon et al., 1999; Nedunuri et al., 2020). These two conventional SCMs concrete have been proven to manage concrete densify via pozzolanic reaction and latent hydraulic reaction. Moreover, their Al phase contribute to increase chloride binding capacity by forming large quantities of hydration products like C(A)SH (Thomas, 2011).

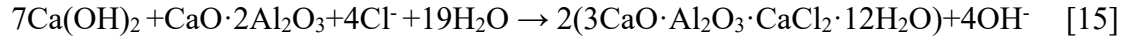
4) Calcium-alminate type admixture: $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA2)

$\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA2), the second principal anhydrous phase in calcium aluminate cement (CAC), is understood to be weakly hydraulic (Sorrentino, 1995). In recent years, CA2 has been developed as a mineral admixture for chloride attack countermeasures (Tabara et al., 2010 and 2013; Mori et al., 2010). The hydration process of CA2 in the Portland cement system generally contains two parts, one of which is the hydration reaction with water to form the main hydration products of CA2 encounters the C_xAH_y phases, and it depends on the curing temperature and cement dosage to generate the phase of CAH_{10} , C_2AH_8 , and C_3AH_6 (Scrivener et al., 1999; Bensted J, 2002). Additionally, CA2 also can react with $\text{Ca}(\text{OH})_2$ to generate hydrocalumite of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 12\text{H}_2\text{O}$ (C_4AH_{13}), which possesses a common substances of structure interlayer between plate crystals of $[\text{Ca}_2 \cdot \text{Al}(\text{OH})_6]^+$ to OH-AFm phase (Bensted J, 2002). The C_4AH_{13} can bind chloride ions by ion exchange to form a more stable phase of Friedel salt (Tabara et al., 2013), whose conservation is similar to the OH-AFm phase. The CA concrete has been confirmed that the chloride binding capacity has been improved with the increased CA2 replacement ratio (Tabara et al., 2010). Moreover, the process of CA2 to form of AFm consumes calcium hydroxide preventing the CH leaching. Therefore, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ is a promising additive for enhancing the chloride resistance of concrete by amplifying its capacity to chemically bind chloride ions. Another appealing point of this material is that with minimal substitutions of OPC (less than 10%), hence concrete manufacturing plants do not necessitate special facilities such as storage tanks. The chemical processes described above, by which CA2 promotes chloride binding in cementitious systems, are summarized in the Equations [13-15].





, which is



CA2 additive significantly enhances the chloride binding capacity of concrete, primarily through the formation of AFm phases to incorporate chloride ions into their crystal lattice to form Friedel's salts. This effect is akin to that of C₃A, and it becomes more pronounced with an increased CA2 replacement ratio (Tabara et al., 2010; Miyazaki et al., 2021; Yunsu et al., 2018). However, the stability of all C_xAH_y phases, which are the hydration products of CA2, eventually convert from thermodynamically metastable to stable mixtures of C₃AH₆ and AH₃ at the curing temperature beyond 30 degree or during the long-term time (Glasser et al., 1999). In a severe environment, the morphological changes of the inner concrete structure may yield a problem with increased porosity and the loss of strength (Ukrainczyk, 2010). The high curing temperature may help CA2 forms products of the final version to cope with the volume change between the product conversion. Consequently, the steam-cured CA concrete may grow into concrete products against chloride attacks with a high industrial value. It is reported that concrete mixed with CA2 as mineral admixture after standard water curing exhibited elevated chloride binding and then increased the threshold chloride concentration under natural seawater environment (Azuma et al., 2017). However, the performance of concrete incorporating CA2 after steam curing as well as the resistance to chloride penetration under cold region's seawater remain unknown.

1.4 Corrosion Monitoring of Steel Bars by Half-cell Potential Method

The corrosion on the surface of the steel bar is an electrochemical process of converting the ions in the pore solution and the electrons in the steel bar (Enevoldsen et al., 1994; Rodriguez et al., 1994; Angst et al., 2011). When steel corrosion starts forming a closed circuit, a sudden release of electrons could cause a shift in an electrical signal (potential or current). This point can be utilized to detect the likelihood of corrosion activation in steel bars within concrete (Elsener et al., 2003; Stratmann, 1990; Wang & Sugiyama, 2022). However, the embedded steel bars in a concrete cover are challenging to measure directly, a known reference electrode is used as a standard to compare the relative potential being a half cell potential to assess the state of the steel bars. Moreover, the complexity of the interior of the concrete considerably affects the value of the half-cell potential (Stratmann, 1990). The potential change can reflect the corrosion state that refers to ASTM C876 standards but cannot express the corrosion rate (Gu & Beaudoin, 1998; Elsener et al., 2003).

Half-cell potential could evaluate of the corrosion of steel bars into two stages (Elsener et al., 2003). The first stage is the onset of corrosion, but its relatively small range of occurrence is too hard to precisely diagnose by normal corrosion monitoring, especially for pit corrosion. The second stage is corrosion propagation, in which corrosion of steel bars can be determined visually as well as empirically. Half-cell potentials are widely used in the corrosion detection of normal concrete, but little is known about the corrosion status of high-strength SCM concrete slabs with a thick cover.

1.5 Research Objectives

Reinforced concrete structures exposed to marine and de-icing salt environments face long-term exposure, with the accumulation of chloride ions increasing the risk of corrosion, which may not be readily apparent on the concrete surface. The deterioration of reinforced concrete structures caused by chloride attack is currently one of the most critical issues worldwide. For long-standing infrastructure, various forms of deterioration can occur over their extended service life even with excellent maintenance. In the case of such structures, precast concrete elements have gained attention due to their sustainability and industry value. With a favorable perspective on precast concrete, it facilitates the replacement of deteriorated components, rather than collapsing the entire system and thereby effectively extending the overall lifespan of the structure. However, the current research on the performance and durability of precast concrete remains relatively limited. Steam-cured concrete is currently one of the widely used types of precast concrete, and it can nearly meet the target strength requirements at 14 days. Additionally, concrete subjected to short-term steam curing attains sufficient strength upon demolding, capable of withstanding challenges posed by transportation immediately. However, there are some contentious issues associated with steam-cured concrete, such as weaker later-stage strength and a coarse internal pore structure that may impact its durability (Kjellsen et al., 1991; Escalante-Garcia & Sharp, 1998; Zain & Radin, 2000 and 2001; Zeyad et al., 2022, Yang et al., 2014). Consequently, SCMs

are being utilized in steam-cured concretes with hope to enhance the long-term durability and later compressive strength, just as effective functions have already proven the worth in standard-cured concrete. Nevertheless, research on SCM steam-cured concrete in engineering is urgently lacking. Furthermore, as more SCM varieties are continuously developed to address specific forms of deterioration, adding calcium-aluminum additive (CA2) to concrete in highly saline environments is considered a viable and effective method for controlling chloride diffusion. Despite the promising potential of CA2 in ordinary concrete, research on the chloride resistance of steam-cured CA concrete in cold-region marine environments is limited.

In accordance with the unclear behavior of steam-cured SCMs concrete, the detection of steel corrosion in a thick concrete cover presents a significant challenge due to the uncertainties within the interior of high-strength SCM concrete. Furthermore, in the case of reinforced concrete bridge slabs exposed to de-icing salt, the freeze-thaw cycles and potential ASR threats are likely to occur concurrently with chloride attack. Research on steam-cured concrete slabs experiencing this combined damage is crucial for the safe use of precast concrete for the bridge slabs.

This dissertation aims to address these issues by conducting experiments to investigate the chloride resistance of steam-cured SCMs concrete in cold-region marine environment and deicing salt condition. Also, it gives the evolution of pore structure in steam-cured SCMs concrete with time and the apparent chloride diffusion coefficient (D_c) during exposure in the field for one year. Resistance of steel corrosion in the high-strength steam-cured SCMs concrete has managed to diagnose properly by the electrochemical technical method. In summary, the purpose of this study mainly focuses on the following issues:

1. To assess the chloride resistance of CA concrete subjected to steam curing in a cold-region marine environment, the performance of steam-cured concrete incorporating fly ash and blast furnace slag is also examined for comparison using the apparent chloride diffusion coefficients (D_c).
2. To explore the evolution of pore structure in steam-cured SCMs concrete during a one-year exposure to seawater in a cold region, the experiment utilizes Mercury Intrusion Porosimetry (MIP) for assessment.
3. To investigate the enhancement of resistance against chloride-related corrosion by inhibiting the chloride penetration in high-early-strength steam-cured SCMs concrete to mimic a concrete bridge slab exposed to deicing salts condition. Furthermore, the corrosion resistance of steam-cured fly ash concrete is studied in the presence of combined damage resulting from ASR and chloride attack.
4. To explore the feasibility of utilizing the half-cell potential method for diagnosing steel corrosion in double-layer steel bars embedded in high-early-strength steam-cured SCMs concrete with a thick concrete cover.

1.6 Thesis Structure

This thesis is consisted by four chapters includes of two main experiments; the outline shows on Figure 1.3.

Chapter 1 briefly introduces the relevant background knowledge involved in the next two main chapters. It presents the context and research purpose of this thesis.

Chapter 2 investigates chloride penetration in steam-cured concrete incorporating supplementary cementitious materials (SCMs) in cold-region marine environments. Normal-strength SCMs concrete was used to investigate the impact of curing methods and binders' properties on chloride resistance. Three curing methods has been employed in normal-strength concrete—standard curing (W), steam-air curing (S), and steam-water curing (SW). A notable finding was the effectiveness of steam-air-cured concrete mixing a calcium-aluminum additive (CA2) on inhibiting chloride diffusion, despite the hydration products of CA2 additive may introduce some void in the concrete over a year in seawater, as detected via Mercury Intrusion Porosimetry. Moreover, normal-strength blast furnace slag concrete displayed excellent chloride resistance across three curing methods, while fly ash concrete exhibited a preference for water curing methods. In the high-strength series, SCMs concrete highlighted the predominant influence of water-cement ratio on chloride resistance, surpassing the effects of curing methods and binder types. Consequently, high-strength CA concrete did not show a significant effect compared to the specimens only using cement. Chapter 2 incorporates several data, figures, and graphs presented in “Effect of steam curing on chloride penetration resistance of concrete with supplementary cementitious materials in the marine environment”. Proceedings for 3rd ACF Symposium 2019: Assessment and Intervention of Existing Structures, authored by Wang et al. (2019). Additionally, a journal paper based on this work is currently under preparation for publication.

Chapter 3 based on the conclusions drawn from the chloride penetration analysis in Chapter 2 for high-strength steam-cured concrete, fly ash and blast furnace slag were selected as SCMs to manufacture high-early-strength double-reinforced concrete bridge slabs for enhancing long-term durability, environmental sustainability, and economic feasibility. This investigation aims to further explore the contribution of the improved chloride resistance of SCMs concrete to the steel corrosion resistance in a salt-laden environment through the comparison of the apparent chloride diffusion coefficient and corrode initial time. Moreover, a practical non-destructive electrochemical diagnostic method effectively detected steel corrosion initiation, overcoming interference arising from the thick and dense layers of high-strength concrete during steel corrosion monitoring. In steam-cured concrete containing reactive silica aggregates with a pessimum ratio exposed to deicing salt conditions, the addition of fly ash noticeably postpones upper-layer steel corrosion onset and alleviates ASR deterioration. Chapter 3 incorporates several data, figures, and graphs presented by Wang and Sugiyama (2023) and Wang et al. (2021).

Chapter 4 summaries the conclusions of the dissertation and dicusses the future works.

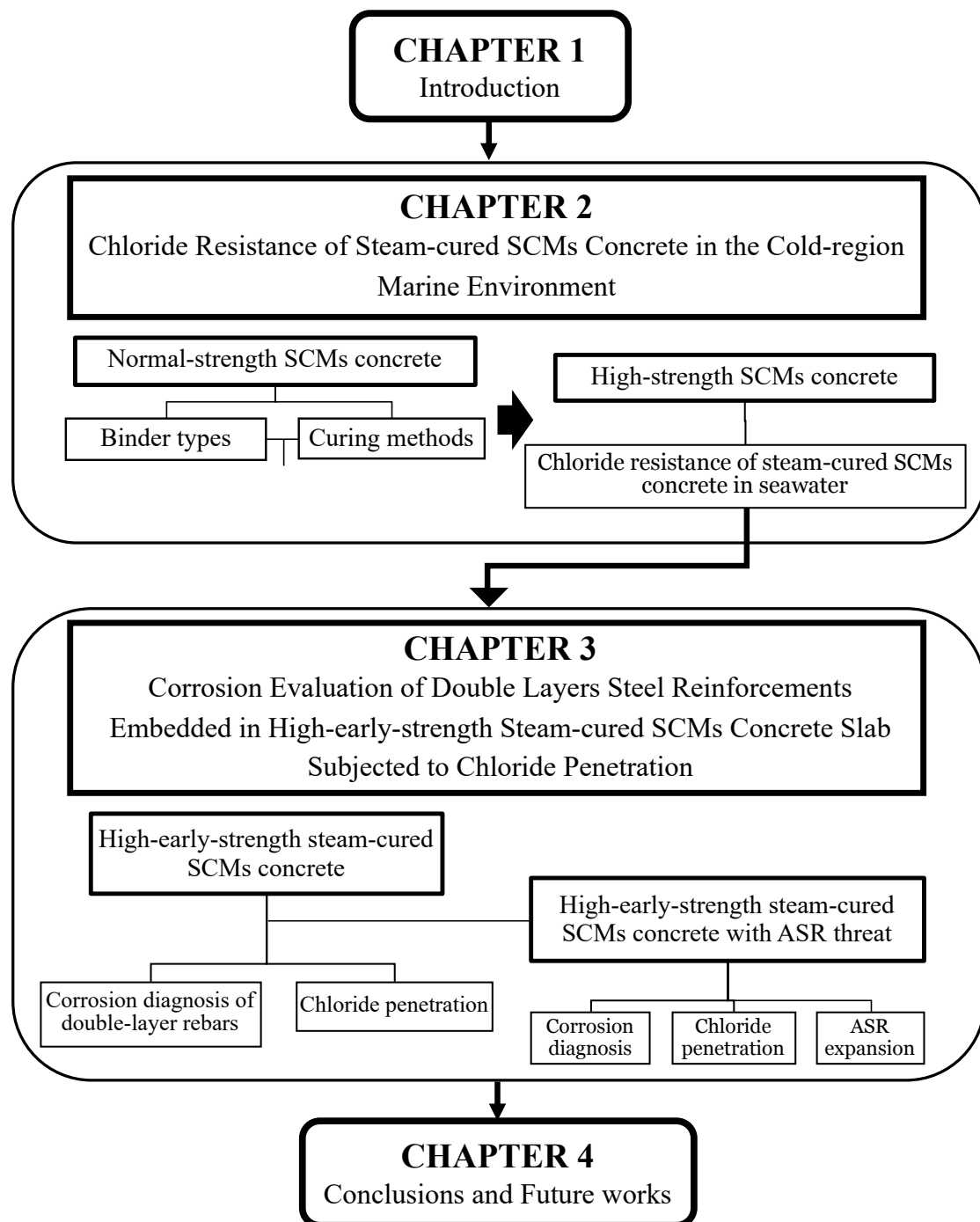


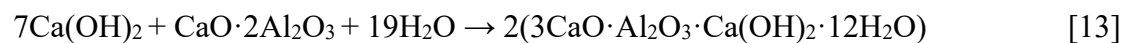
Figure 1.3 Outline of the dissertation

CHAPTER 2

CHLORIDE RESISTANCE OF STEAM-CURED SCMs CONCRETE IN COLD-REGION MARINE ENVIRONMENT

2.1 Introduction

To ensure that precast concrete products maintain the required level of quality for harsh demanding environments, such as marine environments in cold regions, thorough investigation is necessary. Mineral additives such as fly ash and blast furnace slag have been studied for partial replacement of ordinary Portland cement to increase the resistance to chloride penetration. However, research on the chloride resistance of these two types of SCM concrete subjected to steam curing in cold-region seawater is still insufficient. Recently, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ additive (CA2) is directed to enhance the resistance to chloride penetration in concrete because of its ability to bind chloride ions to form stable solid like Friedel salt (Tabara et al., 2010; Morioka et al., 2010). Therefore, CA concrete is expected superior performance against chloride attacks under salt-laden environments. Theoretical aspects of the reduction of chloride penetration in CA concrete are given in following equations.



Furthermore, one more advantage of CA concrete in industrial production is its minimal storage facility requirements in concrete manufacturing plants due to the low OPC replacement rate.

2.2 Research Scope

Past study has stated that CA concrete exhibited a proper chloride resistance in marine environments (Azuma et al. 2017). CA2 additive in cementitious system shows an increased chloride binding capacity because of its high aluminate content. However, the study on chloride penetration in steam-cured CA concrete in salt environment remains unexplored. This research evaluates the chloride resistance of steam-cured concrete with CA2 additive in cold marine environments, employing the experiment of chloride content measurement. The obtained chloride profiles provide apparent diffusion coefficients (D_c) following Fick's second law. Additionally, the chloride resistance performance of CA concrete is compared to that of conventional SCM concretes containing fly ash and blast furnace slag through D_c . The seawater exposure took place in Hokkaido, where seasonal seawater temperatures range from up to 25 degrees Celsius in summer to as low as 1 degree Celsius in winter. The evolution of pore structure in steam-cured SCMs concrete before and after one-year seawater exposure is also confirmed via MIP analysis.

2.3 Materials and Experiments

2.3.1 Mix proportion

In this research, all concrete mixes were based on a commercially available Ordinary Portland cement (N) conforming JIS R 5210. SCM concretes incorporated with three mineral admixtures with different replacement ratios, individually. Low calcium fly ash (FA) conforms with JIS A 6201 type II with the density is 2.27g/cm³. Blast furnace slag (SG) is compliant with JIS A 6206 standard with a specific surface area of 4,000 m²/g and 3.18g/cm³ for density. The concrete was mixed with a calcium aluminate additive with a density of 2.97g/cm³ (CA2), replacing the mass of cement at 7%, with the aim of adding aluminate content to the concrete system. The fine aggregate employs river sand with a density of 2.69g/cm³ and absorption of 1.78%. The coarse aggregate is crushed stone with a maximum particle size of 20mm with a density of 2.66g/cm³. The CA2 additive shares the same chemical composition as that of Miyawaki (2021), with a density of 2.69g/cm³. It exhibits a mass of around 24.0% for CaO, 67.7% for Al₂O₃, 7.1% for Fe₂O₃, and only 0.6% for SiO₂. Tupole EX50 as AE water-reducing agent conforms to JIS A 6204 water-reducer standard type (Type I). AE-300 agent entrains the required amount of air into concrete and fits JIS A 6204 AE agent (Type I). Additionally, two compressive strengths of concrete were conducted by designed strength of 24 N/mm² (W/B is 50%) and 50 N/mm² (W/B is 34%) were denoted as “24-series” and “50-series”, respectively. The microstructure and chloride resistance of concrete are discussed among four types of concrete mixes, two compressive strength serials, and three curing methods. Mix proportions are shown in Table 1.

Table 1 Mix proportions of 24 series and 50 series

Series Type	W/B (%)	Replacement ratio (%)	Slump (cm)	Air content (%)	s/a (%)	Unit (kg/m ³)									
						Water	Cement	Sand	Gravel	Fly ash	CA2	Blast furnace slag	EX50	AE-300	
24	50	N	-	12±	5.0±	153	306	867	1006	-	-	-	2.90	2.14	
		FA	15			46	149			254	44.8	-	-	2.84	3.58
		CA	7			153	284			-	21.4	-	2.74	1.83	
		SG	50			150	150			-	-	150	1.95	1.50	
50	34	N	-	2.5	1.5	150	441	764	1001	-	-	-	5.74	3.53	
		FA	15			43	146			365	64.4	-	-	5.15	5.15
		CA	7			150	409			-	30.8	-	6.16	3.52	
		SG	50			147	216			-	-	216	4.96	2.59	

2.3.2 Specimens preparation

1) Specimens preparation

The casting procedures and the dimension of specimens for corresponding experiments followed the Japanese industrial standards (JIS). The curing method includes steam-air curing (S), standard curing (W), an additional method, steam-water curing (SW), aims to investigate the effect of the water supply on pore structure development after steam curing. The number of concrete specimens is listed in Table 2 according to the type of experiment. The steam curing progress are present in Figure 2.1, and the curing process of three curing methods before experiments for seawater exposure are displayed in Figure 2.2. To avoid the thermal cracks generated in concrete, the increase rate of temperature was set at 15 degrees per hour. The maximum steam-curing was 50 degrees, which aspires concrete to prevent potential damage of delayed ettringite formation (DEF) and meet the labor and economic purpose (Hime, 1996; Cassagnabère et al., 2009; He et al., 2012). Subsequent mixing, the specimens for the compressive strength experiment were cast into cylindrical plastic containers (diameter 100 mm, height 200 mm, JIS A 1132). The test conducts on one day (only for steam-cured concrete), three days (only for standard-cured concrete), 14 days, 28 days, 91 days, and one year. Applied specimens exposed to seawater was a cube with a side length of 100 mm. The cube specimen was sealed with waterproof resin and only left two opposite surfaces used for one-way diffusion when the concrete was under chloride penetration. The exposed surfaces of the specimens to seawater are the surface unmolded during the steam curing and the corresponding opposite side.

Table 2 Experiments and specimens for 24 series and 50 series

Experiments	Dimension of specimens (mm)	Experiment intervals	Curing methods	Total specimens	
				24 series	50 series
Compressive strength	$\phi 100 \times h200$	1d (S, SW), 3d (W), 14d, 28d, 91d, 365d	W, S, SW	45	30
Chloride Content	$100 \times 100 \times 100$	3, 6, 12 Months	W, S, SW	48	32
MIP (24 series)	Same specimens for Chloride content test	Before seawater exposure	W, S, SW	-	
		After seawater exposure	S		
EPMA	Same specimens for Chloride content test	24series 3M, 6M 12M	W, S, SW(6M)	-	
		50series 3M, 6M	W(12M), S		
Surface permeability (24 series)	The specimens for Chloride content test	14 days	S	-	
		28 days			

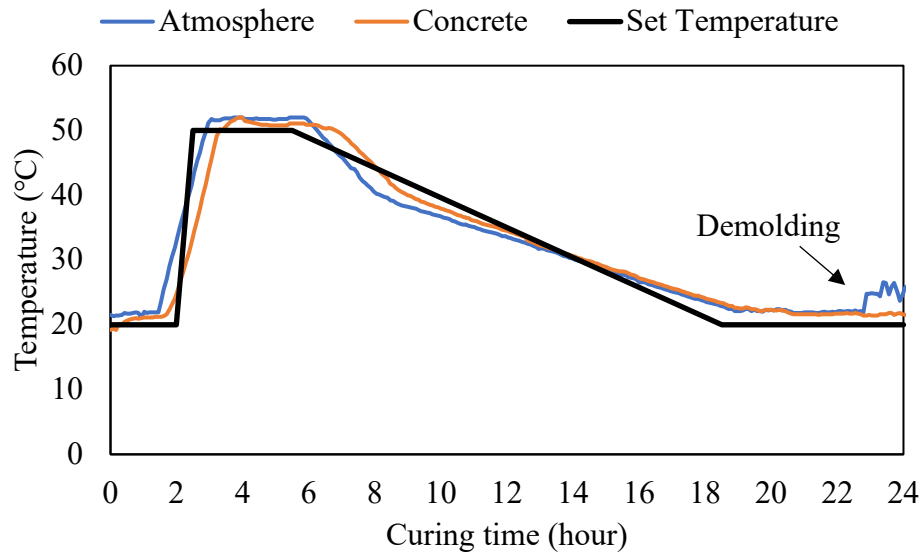


Figure 2.1 Steam curing set and the temperature in concrete

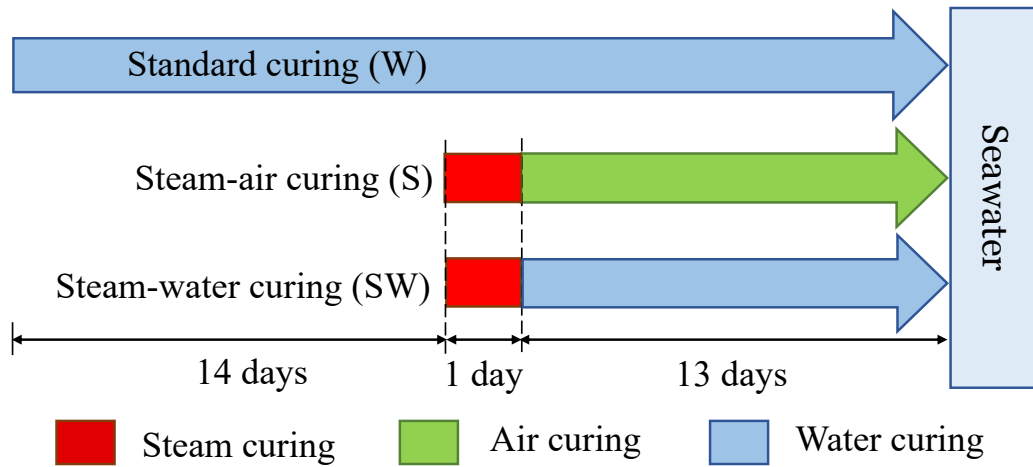


Figure 2.2 Processes of three curing methods before seawater exposure

2) Seawater exposure site

In this experiment, the experimental specimen is fully immersed in fresh seawater continuously pumped from the sea, as depicted in Figure 2.3. The seawater exposure site is situated at the Usujiri Fisheries Station, Hakodate campus of Hokkaido University, Japan. Hokkaido belongs to a cold region, with sea temperatures near Hakodate coast remaining below 10 degrees Celsius for more than six months annually, with approximately three months falling below 5°C, as illustrated in Figure 2.4. These low temperatures delay the hydration process of Supplementary Cementitious Materials (SCMs) and cement particles, concurrently impacting chloride penetration within the concrete specimens. Additionally, the intricate composition of seawater may potentially influence the stability of compositions within the concrete.

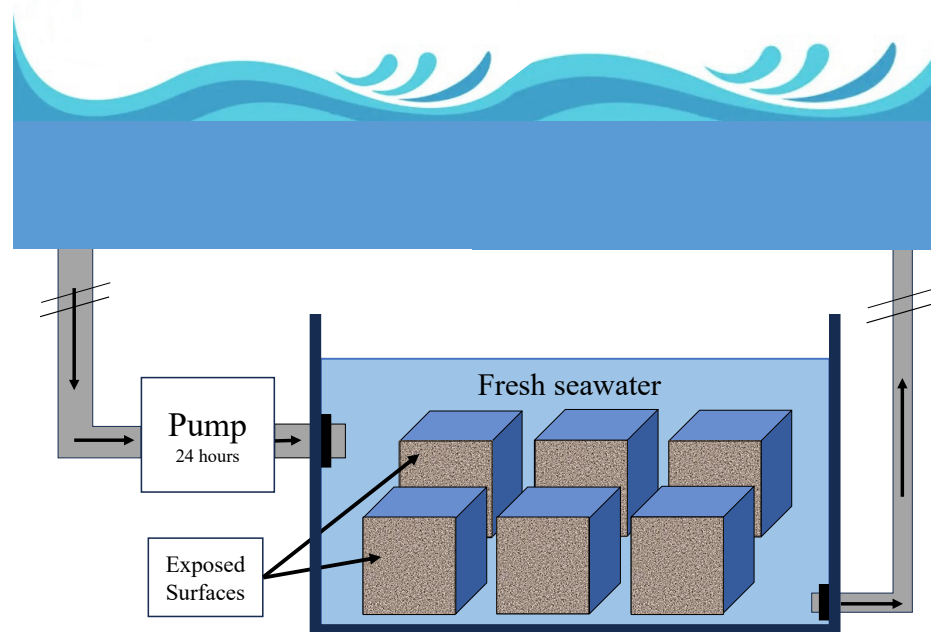


Figure 2.3 Seawater exposure site in Hakodate, Japan

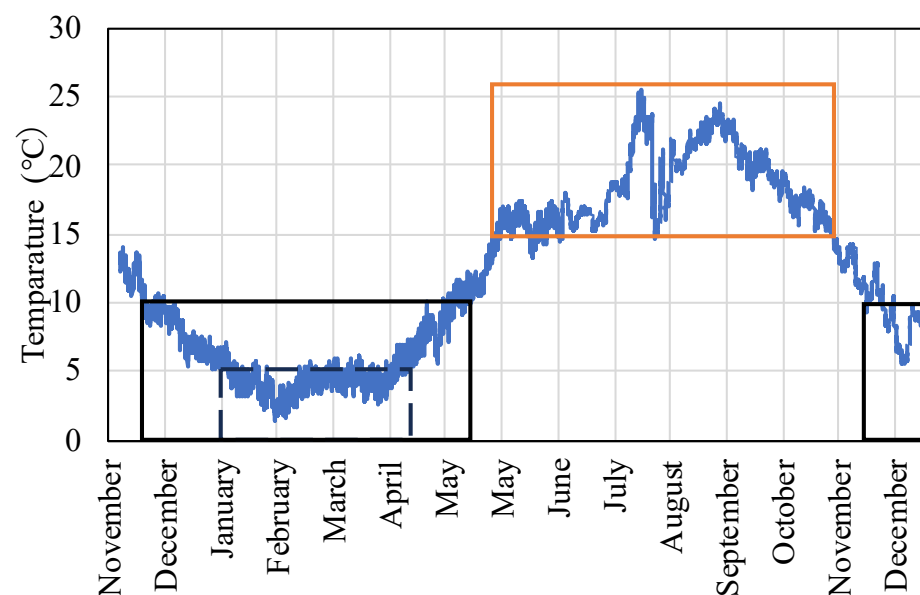


Figure 2.4 Seawater temperature variation from November 2018 to December 2019

2.3.3 Methodology

1) Water permeability of concrete surface

As an experiment to evaluate the water tightness of concrete surface as the index for surface quality using the Nondestructive Inspection Method of Double-Chamber Water/Air Pressure Permeability Tester (WAPP) to gain the surface water permeability coefficient of 24S concrete (Toyofuku et al., 2015). Furthermore, the influence of the quality of concrete surface on chloride penetration is considered. The test was carried out at ages of 14 days and 28 days (the last 14 days are water curing). The surface permeability coefficient on 14 days and 28 days as shown in the Table 3. The permeability coefficient of fly ash was an order of magnitude higher than that of other concrete types at 14 days because of the slower hydration rate of fly ash and the possibility of bleeding. Whereas its permeability coefficient dropped to the minimal after 14 days of water curing, followed by 24CA and 24SG.

Table 3 Surface water permeability coefficient of 24 series concrete

	Average surface permeability coefficient (m/s)	
	14 days	28 days (Water curing after 14 days)
24N	1.72E-12	6.44E-13
24FA	1.17E-11	1.26E-13
24SG	2.43E-12	2.92E-13
24CA	4.77E-12	1.39E-13

2) Mercury Intrusion Porosimetry (MIP)

Mercury Intrusion Porosimetry is a classical technique applied to investigate the porosity characteristics, while its origins to use for soil and rock (Laskar et al., 1997; Kumar & Bhattacharjee, 2004; Ye, 2005). Mercury is a non-wetting fluid that relies on incremental pressure to penetrate into pore systems. Mercury is intruded into concrete interior through both low and high-pressure cycles, with a broad pressure range of up to 60,000 psi (414 MPa). However, the “ink-bottle” effect inevitably occurs when mercury intrudes into narrow neck (Winslow et al., 1994; Giesche, 2006). The experiment equipment is AutoPore IV 9500 made by Shimadzu Corporation. The specimens were cut into 5mm cubes, soaked in acetone for 24 hours, and adopted D-dry to a degree of vacuum below 0.02mmHg maintained for seven days. Washburn equation provides the conversion from the applied pressure (P) to the equivalent cylindrical pore diameter (d) given by the equation [16] (Washburn, 1921), mercury surface tension (γ) and contact angle (θ) are used. It corresponds to a typical range of an equivalent cylindrical pore diameter from approximately 3nm up to 100 μ m.

$$Pd = -4\gamma \cos\theta \quad [16]$$

where mercury surface tension (γ) equals to 485 dyn/cm and contact angle (θ) is 130°.

3) Total chloride ions content (JIS A1154)

The content of total chloride ions in concrete was measured at three months, six months, and one year. Concrete specimens were removed from seawater and transferred to the laboratory of Hokkaido University for subsequent sample preparation and total chloride content testing. In the process of sample making, it was to be cut into small test pieces with a thickness around 1cm and a square cross area with length width of about 3.5cm. Slight variations in actual specimen dimensions may occur due to unavoidable thickness losses from the cutting tool. After cleaning the sample surface with moist cotton, grinding, and pulverization for chloride ions extraction. The operation is in accordance with JIS A1154. The sample diagram is shown in Figure 2.5.

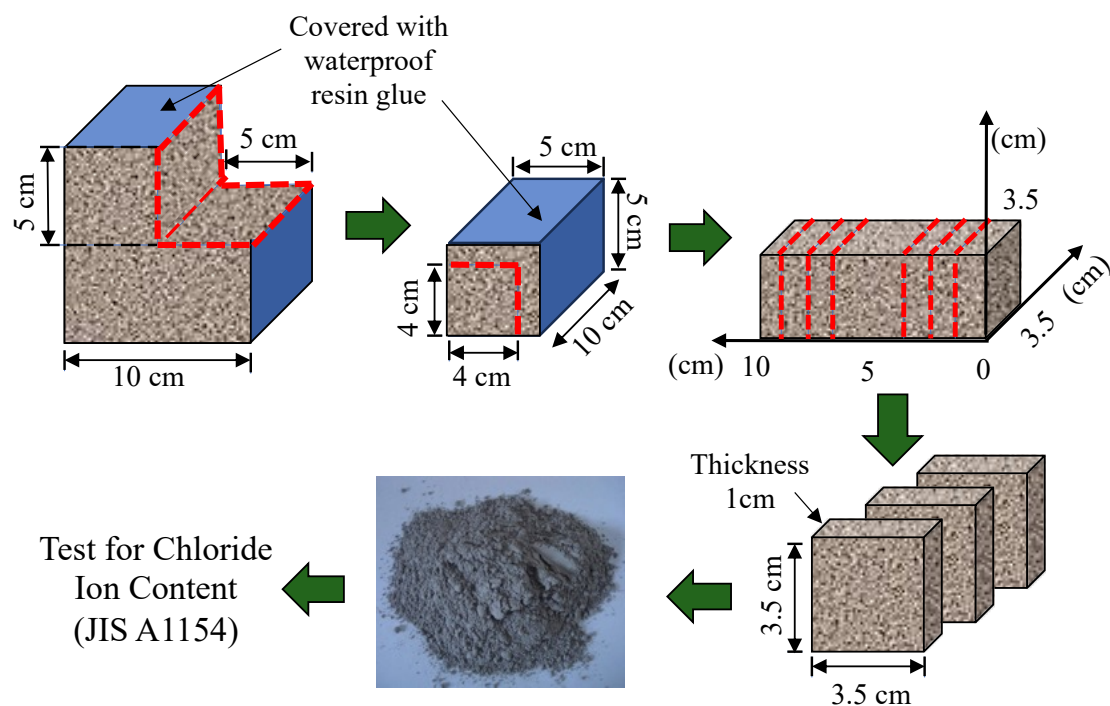


Figure 2.5 Sampling processes for chloride content measurement in concrete

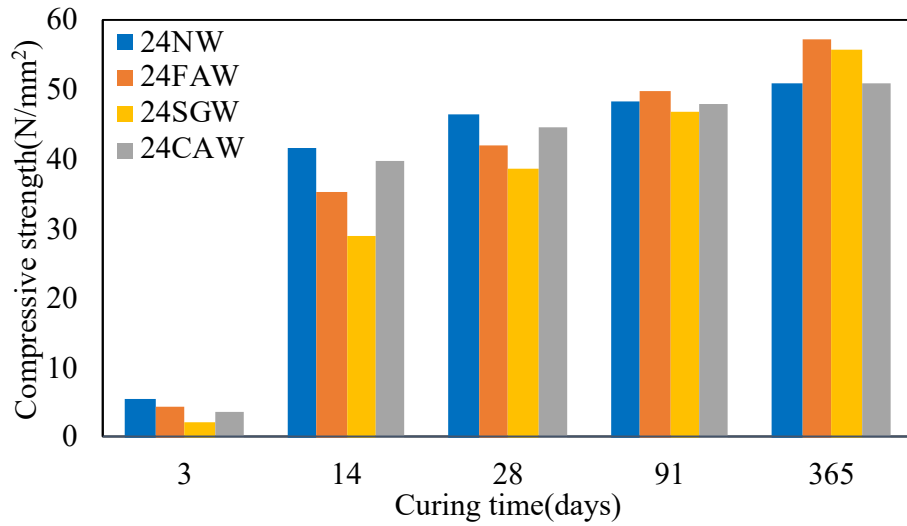
2.4 Compressive Strength of Steam-cured SCMs Concrete

2.4.1 Compressive strength of normal-strength SCMs concretes

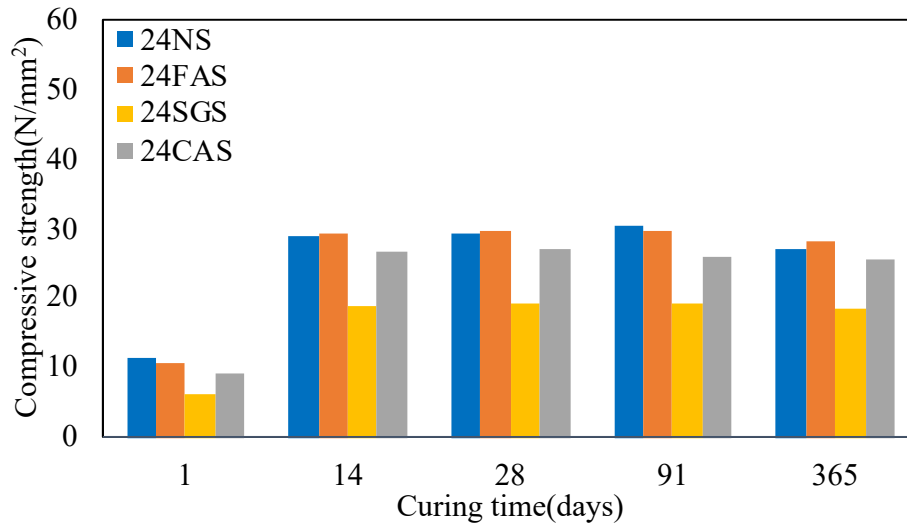
Compressive strength is a fundamental property of concrete. Figure 2.6 illustrates the compressive strength of four types of concrete under three different curing methods. In all types of concrete specimens, the one-day strengths of the steam air curing in the 24S series surpass the three-day strengths of water curing in the 24W series. Regarding the standard curing method in the 24W series, 24FAW and 24SGW initially exhibit lower strength due to the delayed secondary hydration of the supplementary cementitious materials (SCMs). However, they eventually surpass it in terms of long-term strength due to the occurrence of pozzolanic reactions and latent hydraulicity. 24CAW and 24NW display comparable strength values, suggesting that a 7% cement replacement with CA2 has minimal impact on strength.

Specimens from the 24S series were subjected to air curing following one day of steam curing. Consequently, the strength development of all four concrete types stopped after 14 days. The compressive strength of 24NS, 24FAS, and 24CAS reached the designed value at the 14 days, while 24SGS exhibited approximately of 18~19 N/mm². 24CAS presents a rare influence of compressive strength compared with 24NS. In the case of the steam curing followed by air curing in the 24S series, concrete specimens achieved higher strength values on the first day but exhibited retarded growth due to inadequate humidity.

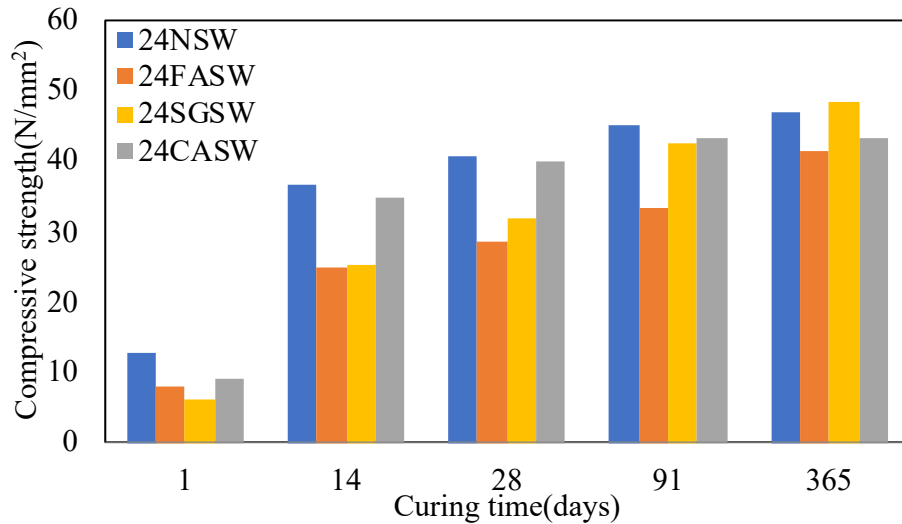
24SW series emphasizes the role of post water curing in cement hydration for concrete subjected to steam curing on the first day. The first-day strength in the 24SW series should match that of the 24S series, while the strengths of the four concrete types in the 24SW series meet the 24 N/mm² strength requirement at 14 days due to water curing. 24FASW shows a restrained strength gained compared to the 24FAW at one year, while the growth trend of compressive strength of 24FASW shows higher ratio than that of 24FAW after 28 days. It is revealed that the pozzolanic reaction in 24FASW may have been restricted by the influence of steam curing, limiting the strength initially, but it potentially has more room to develop in the long term. A related result showed on 24SGSW that its strength growth rate at about 34% after 28 days, which is higher than that of standard curing. This indicates that steam curing provides more hydration potential for fly ash and blast furnace slag in later stages if adequate water curing method is provided. 24CASW shows a constantly similar compressive strength with 24NSW at 14, 28 and 91 days of ages, which is probably because of the less replacement of OPC. Nevertheless, the strength in one year diminished slightly, which may attribute to the hydration products of CA2 converting to the final form. The strength development of 24SW series for one year, the strength of 24NSW, 24CASW, and 24SGSW reached above 90% of the corresponding sample in 24W series, indicating that the steam cured SCMs concrete has expected results in compressive strength aspect when the water curing was properly implemented.



(a) Compressive strength of 24W series



(b) Compressive strength of 24S series



(c) Compressive strength of 24SW series

Figure 2.6 Compressive strength of 24 series under three curing methods over one year: (a) Standard curing (24W), (b) Steam-air curing (24S), and (c) Steam-water curing (24SW)

2.4.2 Influence of steam curing on the compressive strength development of normal-strength SCMs concrete

It is widely recognized that steam curing has an impact on the internal structure of concrete to be coarse. Building upon this understanding, the main focus of this section is to explore whether steam curing has further implications for the cement hydration with SCMs in terms of compressive strength. Figure 2.7 was prepared to analyze the influence of different SCMs and curing methods on the compressive strength, where the x-axis represents the dates of strength measurement, while the y-axis represents the strength ratio of SCMs and N under the same curing method. It should be noted that the 24S series concrete exhibited a retard of strength development after 14 days and longer ages due to the lack of humidity.

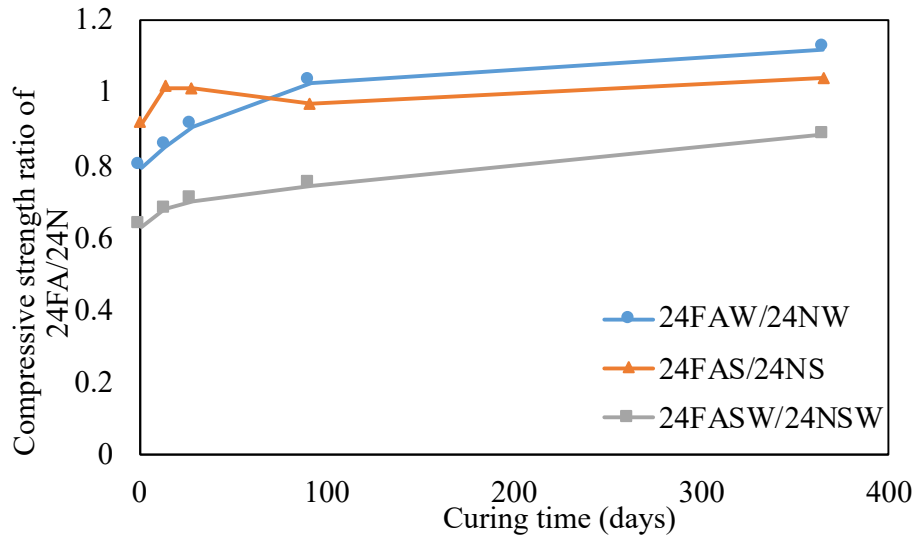
The strength ratio of 24FAW/24NW curve shows a continuous increase from 79.4% to 102.9% with longer ages of from the first day to 91 days and reaches 112 % at one year. It indicates that the pozzolanic reaction of fly ash in standard-cured concrete plays a role in enhancing strength after 28 days. However, the strength ratio curve of 24FASW/24NSW exhibits that 24FASW shows a continuous lower value compared to the 24NSW although the curve shows the upward trend. The 24FASW/24NSW curve reveals a retarded growth of steam curing on the compressive strength development of 24FASW, which also presented in the research from YAZICI (2005). In theory, 24FAS and 24FASW receive identical curing conditions during the steam curing period for the first day. However, notable differences can be observed in the strength development curves of 24FAS/24NS and 24FASW/24NSW with respective strengths of 91.5% and 63.3% at the first day. It could be attributed to individual variations in air content, which were measured at 3.6% and 6.5%. At 14 days, with the strength of 24FAS/24NS increasing by 10%, while 24FASW/24NSW only increases by 4.5%. This phenomenon may be attributed to that adequate humidity promotes the hydration of cement particles more than the pozzolanic reaction. However, the unsaturated water in the capillary pores in 24FAS may support continued hydration with fine fly ash particles rather than the extensive hydration of cement particles. In an environment with sufficient moisture supply, steam curing may have a greater impact on the hydration of cement particles compared to fly ash. As a result, the slower-reacting fly ash particles may become encapsulated within the nuclei formed during the hydration of cement particles, leading to a delayed manifestation of the pozzolanic reaction. In addition, the initial strength of fly ash concrete could be affected by the air content.

The ratio of 24SGW/24NW on the third day of standard curing is lower than that of steam-cured specimens at one day, but it surpasses later one since the ages of 14 days, reaching 97.5% of the strength of 24NW at 91 days. The curve of 24SGSW/24NSW catches up that of 24SGW/24NW closely since the ages of 14 days and reaches 102.6% of 24NSW's strength at an age of 365 days, indicating that the subsequent hydration of the slag in 24SGSW gets hardly affected by the steam curing for the first day. The results of 24SGSW/24NSW and 24SGS/24NS curves suggest that the hydration of blast furnace slag is significantly influenced by moisture rather than steam curing. The

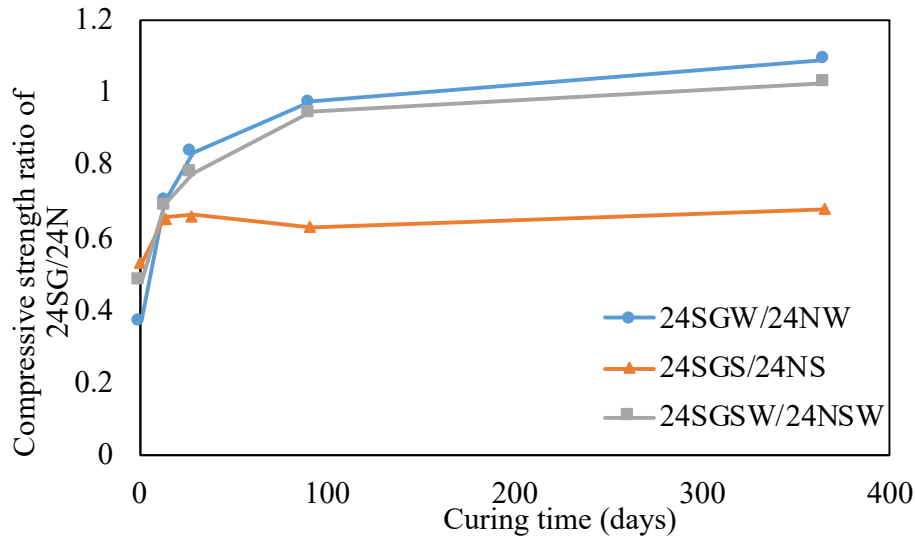
distinct behavior observed in 24SGSW and 24FASW can be attributed to the cement replacement ratio, with 24SGSW providing more hydration opportunities for the blast furnace slag particles because of 50% replacement ratio. It highlights the importance of cement replacement rate as a significant factor affecting the strength development of SCM concrete under steam curing.

For 24CAW/24NW at 91 and 365 days are almost 1.0, which is possibly due to a low cement replacement level. Moreover, CAW concrete shows no contribution to long-term strength development, unlike fly ash and blast furnace slag, as the hydration products of CA2 do not possess cementitious properties. On the other hand, there was a strength decrease observed on 24CASW at one year, in which 24CASW/24NSW shows 98.4% at 28 days and a decrease in the strength at one year with the ratio of 91.5%. This difference may be attributed to the hydration product characteristics of CA2 under different curing conditions. The hydration products of CA2 are temperature-dependent, whose hydration products mainly include the phase of CAH_{10} , C_2AH_8 , C_3AH_6 (after C_xAH_y), and the hydration products formed with calcium hydroxide, such as C_4AH_{13} (Scrivener K L et al., 1999; Bensted J, 2002). With increasing the curing temperature, the hydration products of CA2 in cementitious systems shift from being predominantly C_4AH_{13} to the phase of C_xAH_y . However, the phase transformation among compound of C_xAH_y is associated with the generation of voids over time, for instance, the CAH_{10} may generate 50% of volume change to transfer to the final form of C_3AH_6 . It may explain the variation in the relative strength development between 24CAW and 24CASW.

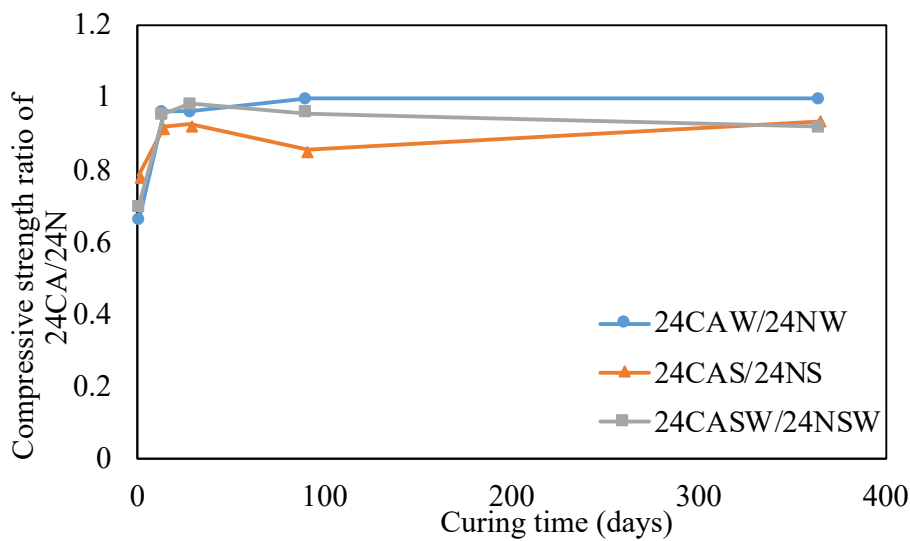
Based on the discussion above, it can be concluded that the steam curing may impose different impacts on compressive strength development of SCM for normal-strength concrete. The relatively slower strength development observed in steam-water cured fly ash concrete may be due to the greater acceleration of cement particle hydration during steam curing. In other words, the increase strength in both the numerator and denominator of the ratio 24FASW/24NSW occurs, but the denominator experiences a more significant increase. This could also lead to an encapsulation effect of anhydrate fly ash particles as nucleation sites for hydrated cement particles. However, the continuous increase in strength suggests that the pozzolanic reaction is ongoing but takes a longer time to manifest. In order to demonstrate the more pronounced contribution of SCMs to strength development, it may be necessary to increase the cement replacement percentage, as seen in the case of 24SGSW. 24SGSW surpasses the reference group at 91 days. On the other hand, 24CASW initially exhibits an identity early strength to the reference group, but a decrease in strength appears after one year. This could be attributed to the phase transition of temperature-dependent hydration products of CA2. Furthermore, subsequent water curing has an improvement effect on the strength development of SCMs concrete after steam curing has been proven.



(a) Compressive strength development of 24FA series under three curing methods



(b) Compressive strength development of 24SG series under three curing methods



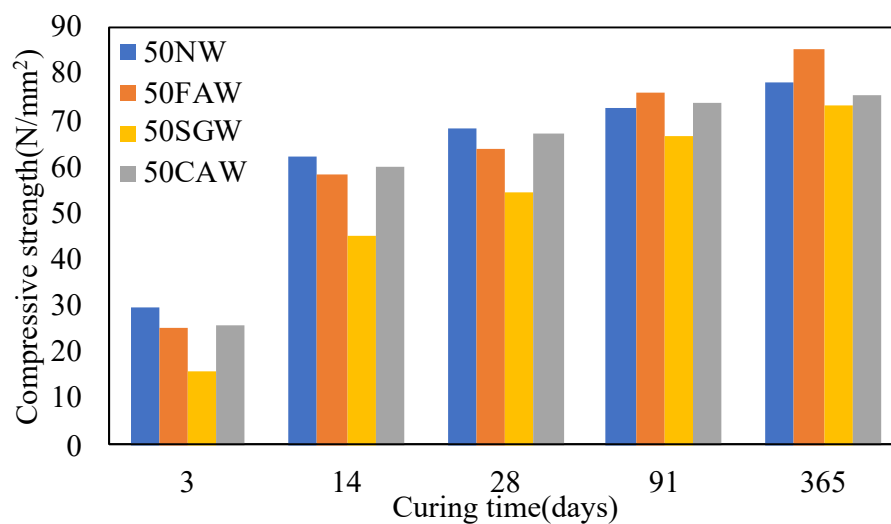
(c) Compressive strength development of 24CA series under three curing methods

Figure 2.7 Compressive strength development of 24series under three curing methods over one year: (a) 24FA series, (b) 24SG series and (c) 24CA series

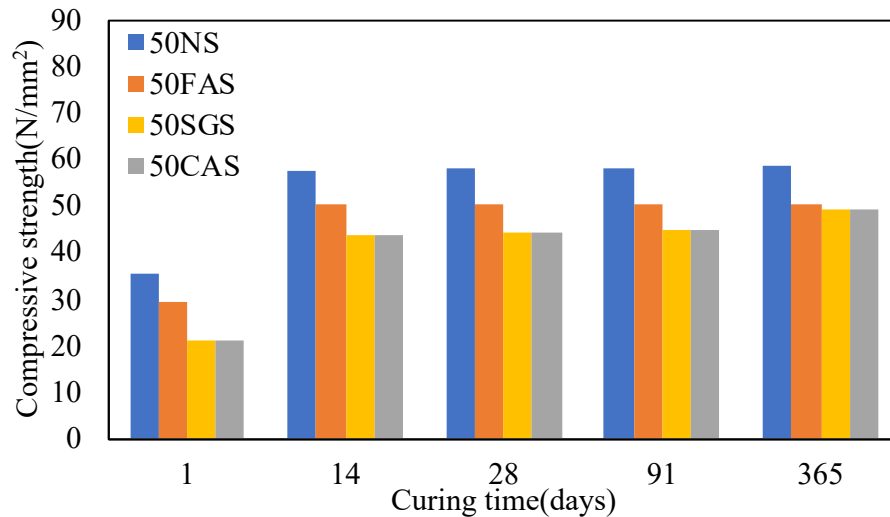
2.4.3 Compressive strength of high-strength SCMs concretes

Figure 2.8 is the strength development in the high-strength concrete serials (50 series) for one year. For all concrete specimens, one day strengths of the steam air curing of 50S series are larger than those of 3 days strengths of water curing of 50W series. The strength of 50FAW that is standard cured fly ash concrete surpasses the strength of 50NW after 91 days and obtains 85.2N/mm² as the maximum strength in 50W series. The strength development of 50SGW is greatly improved after 28 days, although the strength is relatively lower than the control group in one year. 50CAW shows a similar compressive strength with that of 50NW at every curing age, which is similar trend with the normal strength concrete (24CAW).

All SCM steam-cured concretes met the compressive strength to prestressed concretes at 14 days in case of minimum 40 N/mm² as required. Growth rate of the compressive strength of 50FAS and 24FAS are at around 42% and 64% as of the compressive strength at 14 days, while the 50SGS and 24SGS are about 52% and 68%, respectively. The strength growth in high-strength fly ash and blast furnace slag concrete was lower may be because the increased cement usage limited the space for SCMs hydration in the concrete. The strength development of high-strength CA concrete tends to be the same as 24CA concrete under the same curing method regardless of the increased mass of cement usage. The strength reduction in 24CASW for one year does not appear in the high-strength 50CAW concrete, which may indicate that the crystal stability of CA2 hydration products is more stable in high-strength concrete, or the concrete has enough strength to resist the negative impact of the CA2 hydration products in long term.



(a) Compressive strength of 50W series



(b) Compressive strength of 50S series

Figure 2.8 Compressive strength of 50 series under standard curing and steam-air curing over one year

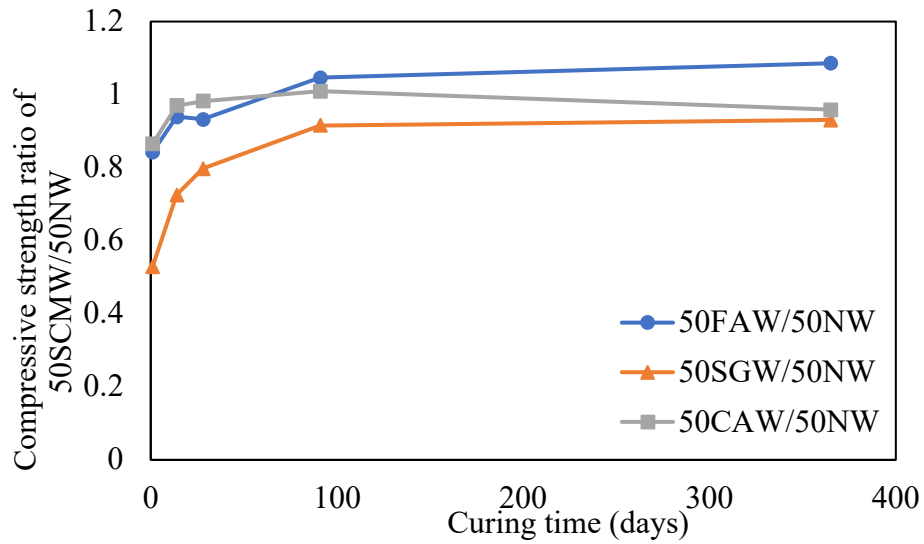
2.4.4 Influence of steam curing on the compressive strength development of high-strength SCMs concrete

For the high-strength concrete series, the strength development trends of SCM concrete under two curing methods compared to their respective 50N series are provided in Figure 2.9. The initial strength for the 50W series concrete was measured at 3 days, while the 50S series concrete under steam-air curing shows the initial strength measurement at the first day.

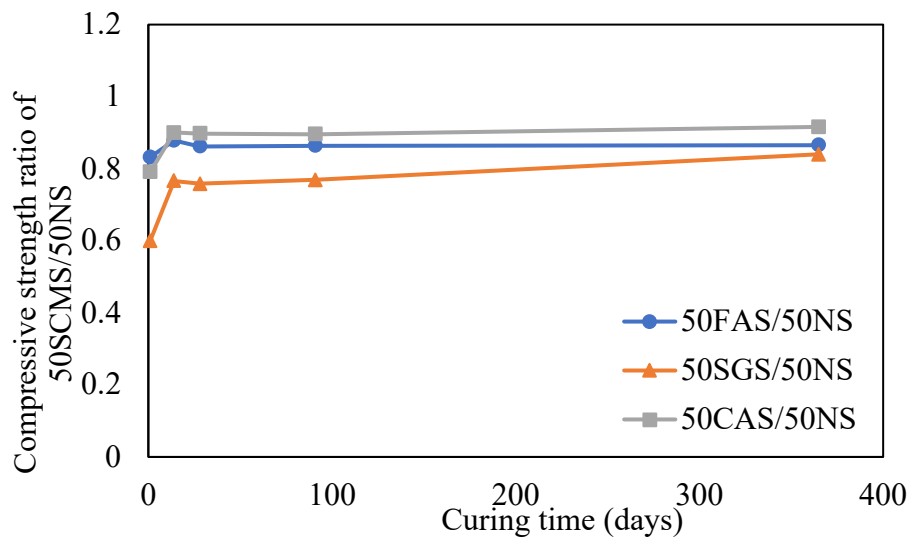
The initial ratio of 50FAW/50NW is 84.3%, which increases to 93.9% at 14 days. The relative stability between 28 days and 14 days indicates that fly ash may experience a partial hydration. At 91 days, the ratio exceeds 100% and continues to increase to 108.5% until 1 year. The upward trend of high-strength fly ash concrete to the reference group and its similarity in terms of normal-strength series (24FAW) suggest that the initiation of significant hydration with fly ash in standard curing may be more related to the dosage portion of fly ash rather than the water-to-cement ratio. The ratio of 50FAS/50NS after steam curing is 83.2%, which increases to 87.8% at 14 days and remains consistent until 365 days because of the low humidity. The 50SGW/50NW curve is initially lower than 50SGS/50NS at 14 days and surpasses it at 28 days. It suggests that the steam curing may have a positive effect on the hydration of blast furnace slag, but the hydration ceases due to water loss. For 50CAW/50NW, the ratio increases from 86.5% to 95.4% from the third day to 14 days, and remains around 100% in one year, indicating that CA2 does not affect the strength of concrete under standard curing. The 50CAS/50NS consistently exhibits relatively lower ratios compared to that of standard curing. Despite the limited moisture content, the strength of 50CAS at 14 days reaches approximately 90% of that of 50NS. This suggests that if water curing is implemented, the later-stage strength of 50CAS is expected to reach a comparable level to that of 50NS.

2.4.5 Influence of water binder ratio (W/B) on the compressive strength developing of SCMs concrete in various curing methods

The relative strength changes of normal-strength and high-strength fly ash concrete, there is almost no difference between 50FAW/50NW and 24FAW/24NW, revealing that the hydration with fly ash in concrete has less influenced by the water-to-cement ratio under standard curing. However, 50FAS/50NS exhibits a higher ratio compared to the 24S series, suggesting a reduced impact of fly ash delaying hydration in high-strength concrete. This could be attributed to a larger presence of hydrated cement particles in high-strength steam-cured concrete, providing sufficient calcium hydroxide to stimulate pozzolanic reactions. The curve trend of 50SGW/50NW before 91 days is similar to that of 24SGW/24NW and 24SGSW/24NW, but the final ratio in one year is lower than that of normal-strength concrete series. This result needs to be considered in relation to the cement usage, where the 50SGW may exhibit a cement deficiency due to 50% replacement level, resulting in a significant strength difference compared to 50NW. In terms of 50FAW, a higher strength ratio is attributed to an adequate cement content compensating for the deficiency caused by the late hydration of fly ash, with the subsequent pozzolanic reaction enhancing the compressive strength for 91 days. Therefore, the influence of different SCM replacement ratios of fly ash and blast on the strength varies for concretes with different W/B ratios. Figure 2.9 shows curves of 50CAW/50NW and 50CAS/50NS overlap with the those of the corresponding 24CAW/24NW and 24CAS/24NS, indicating that the 7% cement replacement ratio has a minimal effect on strength in the concrete having a certain degree of compressive strength. It ensures that concrete incorporating CA2 maintains stability in terms of strength under different water-cement ratios and curing methods. However, the 50CA concretes did not studied for the SW curing method, so it is uncertain whether the potential long-term strength reduction observed in 24CASW would also occur in high-strength concrete of 50CASW. Nonetheless, due to the presence of certain strength in 50CA concrete, it is likely that it can withstand the effects of expansion or phase change caused by CA2 hydration products on strength. Further research is needed to comprehensively understand the impact of CA2 hydration products on the strength.



(a) Compressive strength development of 50W series



(b) Compressive strength development of 50S series

Figure 2.9 Compressive strength development of 50SCM series concrete under standard curing and steam-air curing over one year

2.5 Mercury Intrusion Porosimetry Experiment (MIP)

Extensive research proves that factors such as the water-cement ratio, binder types, and curing period are strongly related to pore structure in cement paste, which could further affect the mechanical properties of concrete in various aspects (Cook & Hover, 1999; Cui & Cahyadi, 2001; Atahan et al., 2009; Halamickova et al., 1995). Steam curing method is biased in terms of their impact on cementitious matrix generating a unique pore structure that compared to conventionally concrete of standard curing (Bentur, 1980). Mercury Intrusion Porosimetry experiment (MIP) is a common method to obtain the information on the pore structure of the matrix of cement pastes. The MIP results could provide the accumulated porosity curve and the pore width distribution curve convey the variation in pore structure of different pastes. In this study, the MIP experiment was carried out only in normal-strength concretes rather than the high-strength series because a relative increased W/C ratio with a higher level of dispersed pore distribution can highlight the roles of the binders and the curing methods on the pore structure. Moreover, the specimens were transferred to expose to seawater for one year after the certain curing in the fore period. The valuable field data would exhibit the evolution of internal pore structures of SCMs concrete suffering the existence of multiple ions in seawater. Particularly, the lab and field data of steam-cured concrete incorporating CA2 is a significant point. However, it is important to note that the interfacial transition zone (ITZ) is a crucial parameter for evaluating concrete properties, yet it has not been provided in the MIP experiment.

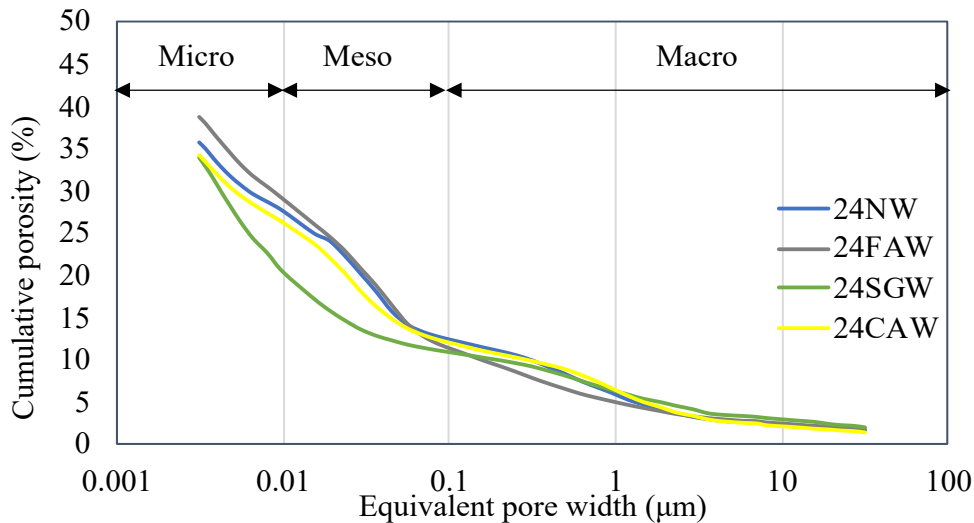
In order to determine the paste volume of the concrete sample under investigation, the volume of acid-insoluble components as aggregates was determined using bulk density measurements. This allowed for the calculation of total porosity and porosity in specific pore size intervals as a percentage of the paste volume.

2.5.1 Mercury intrusion in normal-strength SCMs concrete before seawater exposure

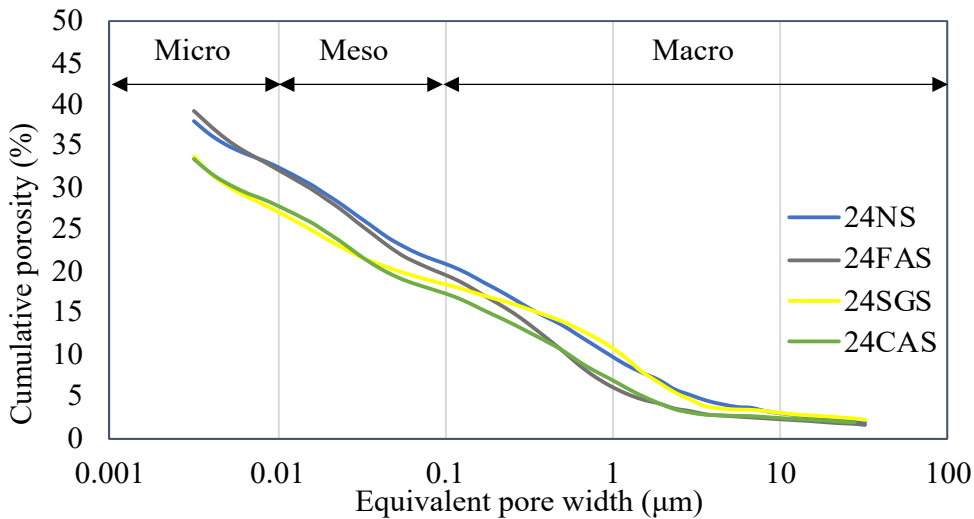
The concrete specimens from the 24W, 24S, and 24SW series undergo marine exposure experiments under their respective curing conditions for 28 days, 14 days, and 14 days of the fore curing, respectively. In this study, the MIP results of the 24W, 24S, and 24SW specimens at 35 days, 26 days, and 19 days are discussed to examine the diversity of the pore structure of SCM concretes under curing methods on “early-stage”. Additionally, after one year of seawater exposure, the 24S specimens were placed in a dry environment until 478 days for MIP testing. The results were presented in Figure 2.10 and Figure 2.11, which show the cumulative intrusion curve (overall porosity or total porosity) and the differential MIP curves as the pore size distribution for standard curing (24W), steam-air curing (24S), and steam-water curing (24SW), respectively.

1) Definition of representatives of the pore size intervals

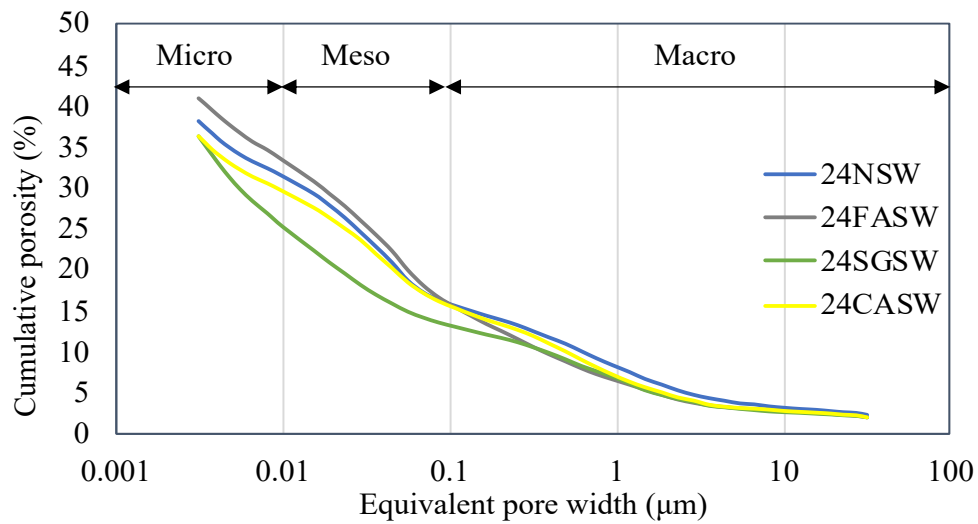
Normal-strength concretes were employed to ensure ample space for the SCMs to exert the characteristics. The total porosity was calculated as the cumulative porosity within the pore size intervals ranging from 3nm to 31500nm. In the majority of cement paste samples, the pore size distribution curves display three prominent regions, namely, pores with widths in the ranges of 3-10nm, 10-100nm, and widths greater than 100nm. Although discussions regarding pore size within the meso-scale range are prevalent (Kumar & Bhattacharjee, 2003; Cui & Cahyadi, 2001), this study naturally classifies into three pore size intervals based on pore size distribution. This also stands as one of the findings of this research. These three pore width ranges correspond closely to the concepts of micropores, mesopores, and macropores in modern concrete research. Therefore, in the subsequent discussions, these terms are used to represent the respective ranges of pore widths within each range is referred to as microporosity, mesoporosity, and macroporosity. Table 4 shows the critical pore size for each concrete types before and after one-year seawater exposure, which means the widest width of interconnected pore pathway in the pores network of the concrete.



(a) Cumulative intrusion curves of standard cured specimens (24W)

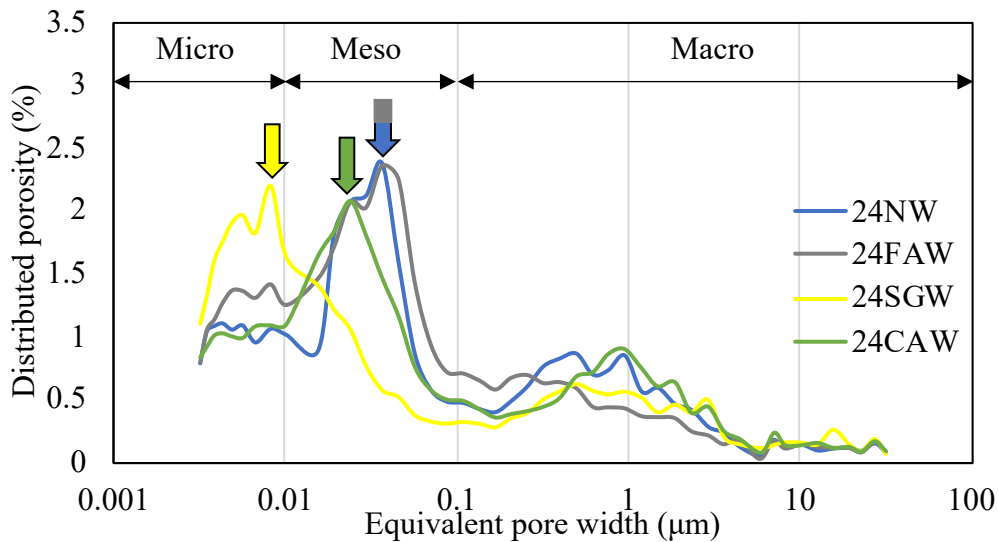


(b) Cumulative intrusion curves of steam-air-cured specimens (24S)

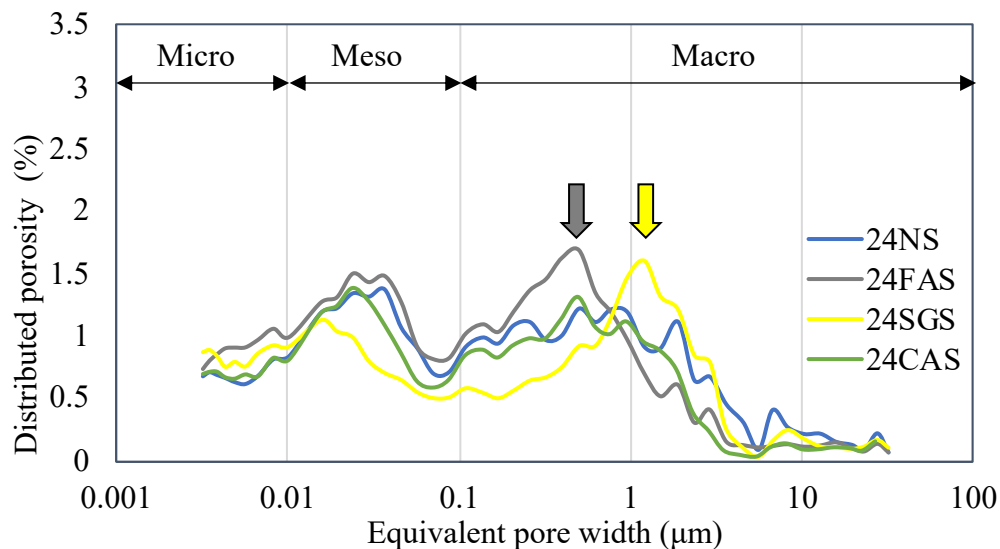


(c) Cumulative intrusion curves of steam-water-cured specimens (24SW)

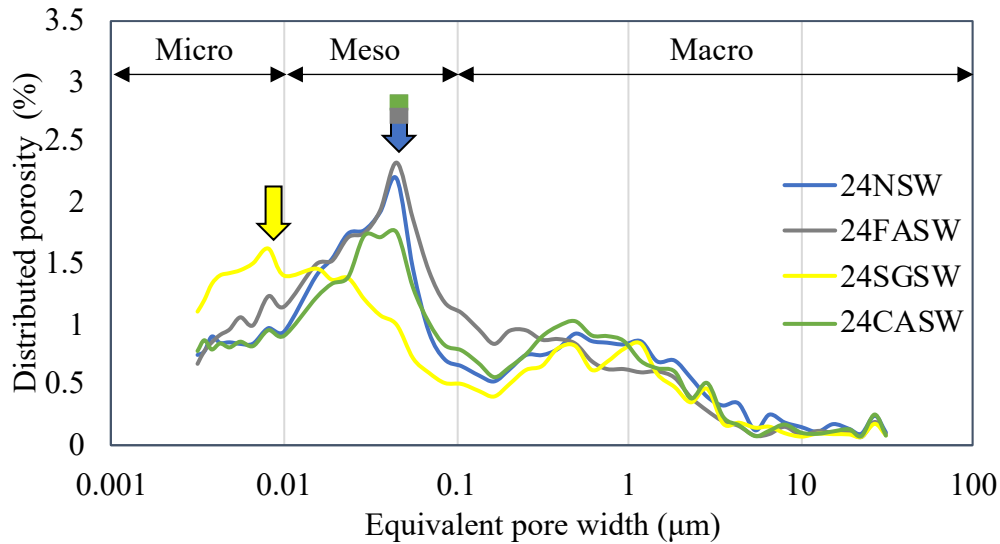
Figure 2.10 Cumulative intrusion curves of four types of 24 series specimens under three curing methods before seawater exposure



(a) Pore size distribution curves of standard cured specimens (24W)



(b) Pore size distribution curves of steam-air-cured specimens (24S)



(c) Pore size distribution curves of steam-water-cured specimens (24SW)

Figure 2.11 Pore size distribution curves of four types of 24 series specimens under three curing methods before seawater exposure

* Arrows marked in each color represent the critical pore size corresponding to the respective curve, with the data matching that in Table 4.

2) Influence of binder types on the pore structure of SCMs concrete under three curing methods

2-1) Standard Curing (24W)

Figure 2.10(a) illustrates that the cumulative intrusion curve of the total porosity of four specimens, which exhibits a gradual increase from flat to sharp as the equivalent pore diameter decreases, while each type of specimen has its distinctive morphology. The total porosity (size of 3nm~31500nm) of specimens 24NW, 24FAW, 24SGW, and 24CAW under standard curing for 35 days was found to be 34.0%, 37.2%, 32.6%, and 32.2%, respectively. The relatively higher total porosity of 24FAW can be attributed to the slower reaction of pozzolanic materials, which is also indirectly evidenced by the fact that its strength behavior on 28 days. The pore size distributions of 24SGW and 24CAW did not show significant differences compared to 24NW, but they exhibited a decrease of approximately 5% compared to 24FAW at 35 days.

The total porosity curve was differentiated to obtain the equivalent pore width distribution curve and distributed porosity in three pore size intervals, as shown in Figure 2.11 and Figure 2.12. Peaks exist in each curve, with the peak at larger pore widths being less prominent compared to the peak at smaller pore widths. Some peaks exhibit the crucial pore size, mostly appear in the pore size interval of 10nm to 100nm. Table 4 includes the critical pore sizes that can exhibit the distinct peak of the pore size distribution curves for all specimens. In contrast with similar total porosities for four types of cement paste, the pore distribution curves show distinctive characterizes at pore size intervals depending on binder type. Four standard-cured pastes at 35 days, the porosity distribution of 24NW, 24FAW, 24SGW and 24CAW in macroscopic range is almost identical, whose portion are 10.6%, 9.48%, 8.87%, and 10.4%, namely. The fly

ash and blast furnace slag sample show that the slight lower portion in this pore width interval due to the refiner characterize of additive materials. Both 24CAW and 24NW show not only a very similar number about macroporosity, but also the pore distribution in this range is comparable. However, in the range of 200 nm to 700 nm, the 24CAW specimen experiences a decrease, which may be attributed to the addition of CA2.

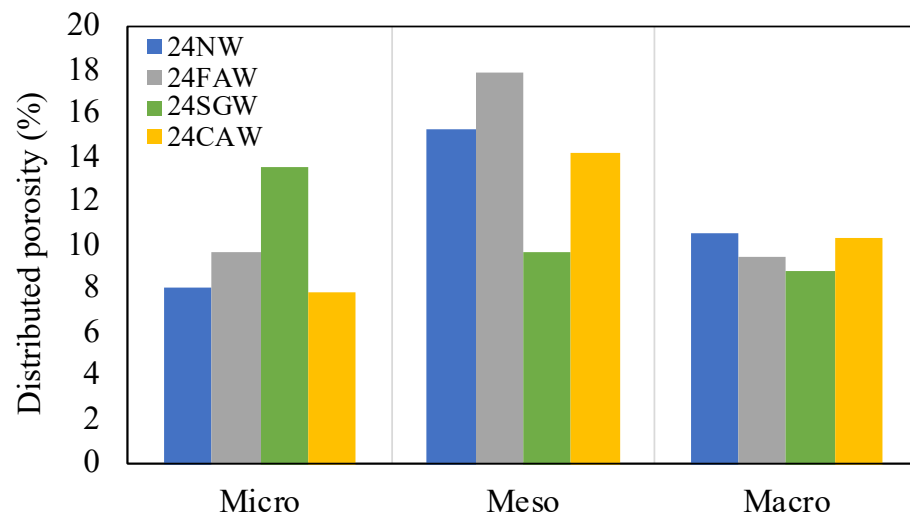
In the mesopores range, 24FAW exhibits the most prominent occupation at 18.0%, followed by 24NW at 15.4% and 24CAW at 14.3%. The mesoporosity of 24SGW is only 9.67%, which is 0.63 times that of 24NW. The main pore distributions for 24NW, 24FAW, and 24CAW are all concentrated in this pore size range, with corresponding critical pore sizes of approximately 40 nm, 40 nm, and 25 nm, respectively. 24SGW has the decrease in the fraction of porosity in this region that may be attributed to the transformation of larger pores into smaller size or closed pores, which could be a result of the refining effect of blast furnace slag in the concrete. Although the fly ash hydration reaction is relatively slow, its filling effect still aids in the transformation of 24FAW from macropores to mesopores. In the case of 24CAW, a refining effect is observed, leading to a leftward shift peak compared to 24NW with a decrease value in the peak. The pore size between 10nm to 100nm in concrete has been investigated by much research that those works definite it as mesopores. While there is currently no well-established theory to explain the transport of substances within the mesopores range, smaller pore sizes can restrict ion movement and offer increased chances for ions to interact with the pore walls of the cement paste. This interaction can potentially lead to a deceleration of ion diffusion in the cement paste (Li & Roy, 1986; Halamickova et al., 1995; Ye, 2005; Atahan et al., 2009).

The pore size below 10nm is generally considered harmless, as they include interlayer pores and encapsulated pores of cementitious products. In this regard, 24SGW has the highest percentage of around 13.6%, followed by the fly ash cement at 9.73%, and 24NW and 24CAW at 8.10% and 7.91% respectively. The majority of the pore distribution in 24SGW is observed within the microscopic range, indicating the brilliant refining effect of the blast furnace slag under standard curing conditions. The higher micropores content in 24FAW compared to 24NW may be attributed to the dense hydration products of fly ash and closed pores. The pore distribution curve of 24CAW shows a close resemblance to that of 24NW, suggesting that the addition of CA2 primarily affects the two distinct pore width ranges in the mesopores and macropores rather than the microscopic range below 10nm.

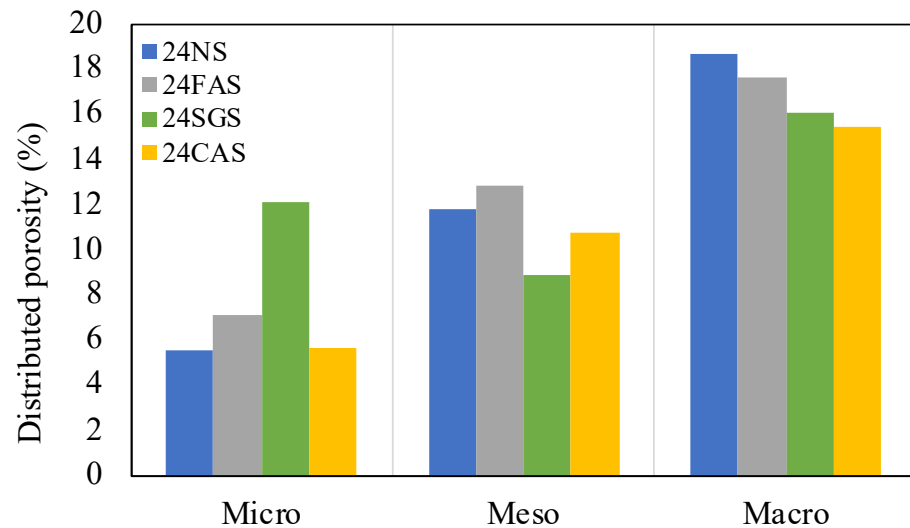
Table 4 Critical pore size in 24 series concrete

	Critical pore size (nm)			
	24N	24FA	24SG	24CA
W	40	40	8	25
S	-*	500	1200	-*
SW	50	50	8	50
S-1Y	20	25	-*	1860

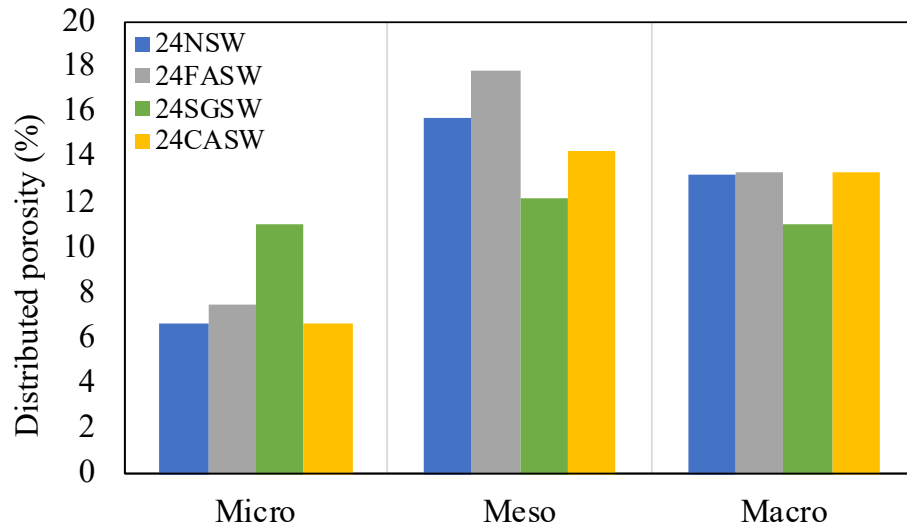
*No distinct peak



(a) Distributed porosity of 24W series



(b) Distributed porosity of 24S series



(c) Distributed porosity of 24SW series

Figure 2.12 Distributed porosity in three pore size intervals of four types of 24 series specimens under three curing methods: (a) standard curing (24W), (b) steam-air curing (24S) and (c) steam-water curing (24SW).

2-2) Steam-air Curing (24S)

The cumulative porosity curves for steam-air-cured concrete did not exhibit distinct inflection points as observed in the 24W series, as given in Figure 2.10(b). Four curves remained relatively parallel across different binder types, especially for 24CAS and 24NS, signaling a close similarity in the pore structure between these two specimens. After subsequent dry curing for 25 days following steam curing, the total porosity of 24NS, 24FAS, 24SGS, and 24CAS was found to be 34.9%, 37.1%, 30.9%, and 30.6%, respectively. Although it has been expected that steam-cured specimens would hold a relatively coarse pore structure, the results show that their total porosity is similar to or even slightly less than that of specimens cured under standard conditions. This phenomenon is particularly evident in the case of 24SGS and 24CAS. The reduction in total porosity can be attributed to the favorable effect of high temperature on the hydration of these two materials, leading to a reduction in total porosity. However, the 24FAS still exhibit slightly higher macroporosity compared to others, which is considered by the delay pozzolanic reaction.

The subsequent discussion focuses on the pore size distribution curves of 24S series in three pore size zones. Four steam-cured pastes that share a notable increase in the proportion of macropores, and a decrease of mesopores and micropores based on Figure 2.12(b), without highlighting binder characteristics. The maximum pore fraction of all steam-air cured specimens is observed within the macropores range that the porosities for 24NS, 24FAS, 24SGS, and 24CAS are 17.9%, 17.3%, 15.5%, and 14.4%, respectively. According to the pore size distribution curves in Figure 2.11(b), the macroscopic pore size distribution curve of 24NS exhibits a uniform distribution of porosity across macropores widths, while 24FAS shows a different trend in the curve with that of 24NS. Moreover, 24FAS is significant mercury intrusion at around 500nm

pore width and generally higher than the other three cement pastes within the range of 750nm. It may indicate that the fly ash has refined a portion of large pores, resulting in a higher porosity at about the peak. 24SGS shows a lower macroporosity, despite having a prominent peak at 1200nm. It may be explained by that the 50% cement replacement in 24SGS can be a double-edged sword, as it generates a higher proportion of large pores, making it difficult for the fine blast furnace slag to fill the excessively wide pore spaces. However, significant refinement effects of blast furnace slag can be achieved within the feasible pore width range, such as within the equivalent pore width of 750nm. On the other hand, the curves for 24NS and 24CAS nearly overlap in macroscopic pore size range with an indistinct peak. The geometric interpretation of the round peak in the curve suggests that as the pressure applied by the MIP device increases, the amount of mercury intrusion may remain constant. This implies that an equivalent amount of mercury could penetrate into smaller pore sizes.

In the pore size distribution graph for pores smaller than 10nm in 24S series, there is no prominent increase like in the case of the 24W series. This phenomenon can be attributed to the rough pore structure caused by steam curing and the inhibition of hydration due to low humidity. Moreover, 24CAS indicates that the refining effect provided by the CA2 is insignificant within this pore size range. Furthermore, 24SGS presents a rise porosity due to the presence of a large amount of blast furnace slag content in the cementitious matrix.

2-3) Steam-water curing (24SW)

Steam-water curing specimens have undergone one day of steam curing and 18 days of water curing. Figure 2.10(c) and Figure 2.11(c) provide a convenient way to observe the cumulative pore curve and pore size distribution curves, and Figure 2.12(c) shows the portion depending on the pore size in four pastes. The total porosity of 24NSW, 24FASW, 24CASW and 24SGSW is 35.9%, 38.7%, 34.3% and 34.3%, namely. In terms of total porosity of four types of 24SW pastes present basically similar, though the 24FASW still shows a relatively higher. It suggests that even with subsequent water curing, the pozzolanic reaction in steam-cured FA concretes are influenced by the elevated temperature. Further discussion is needed based on the pore size distribution curves to provide more insights. On the other hand, the relative higher porosity of 24SW than 24S because of the curing time only for 19 days.

24NSW, 24FASW, and 24CASW show almost identical porosity of 13.3%, 13.4%, and 13.4% in the macroscopic pore range, while 24SGSW exhibits a slightly lower percentage of 11.1%. Observing the curves, four binder types show complex overlap. 24FASW presents a continuous upward trend and gradually surpasses the curves of other binder types at approximately 500nm. This can be seen as a process where the pore size distribution shifts from larger pores to smaller ones, which can be attributed to the reaction of pozzolans. 24SGSW exhibits its curves consistently located at the bottom position beneath the others, which is contributed by hydration of blast furnace slags. In the macroscopic width range, 24FASW and 24SGSW exhibit protrusions rather than the pronounced peaks observed in the 24S series. This indicates that

subsequent water curing can compensate for the traces of rough internal pore structure left by steam curing. The macroscopic pore size distribution curve of 24CASW closely resembles that of 24NSW, suggesting that the 7% of replacement ratio of CA2 material has a minimal effect on the macroscopic pore distribution in the early stages.

The mesoporosity for 24NSW, 24FASW, 24CASW, and 24SGSW are the dominant components in the total porosity of the individual specimen, accounting for 15.8%, 17.8%, 12.2%, and 14.3% respectively. 24FASW and 24NSW show the critical peak at around the pore size of 50nm, which is also observed in the case of 24CASW. The peak observed in 24CASW curve is in a transitional state, and it is likely to evolve towards a sharper and left-shifted peak similar from that of 24CAS to 24CAW. The pore distribution of 24CASW in the 10nm to 50nm pore width range shows a lower porosity compared to 24NSW, indicating that CA2 additive may act an effect on the pore sizes in this range. The second peak in the 24SGSW primarily occurs within the microscopic range. The significant substitution of cement with blast furnace slag in 24SGSW could be the reason for this alteration. 24NSW, 24FASW and 24CASW are observed with no significant increase below 10nm during the subsequent 18-day water curing process, while 24SGSW has started to mitigate the potentially negative effect from the steam curing. Generally, water curing after steam curing supports for continued hydration of the cementitious matrix and refinement of pore structure, which can indirectly impact the development of concrete strength. It is worth noting that while the pore distribution curve of 24SW differs from the same binder type in 24W series, the critical pore size between specimens is similar than 24S series. It may suggest that water curing governs the pore parameter of the critical pore size.

2-4) Post water curing effects on the pore structure of steam-cured SCMs concrete

Hydration development of different binders in cement pastes under different curing conditions can also be discussed. It is evident that the steam-cured cement paste exhibits a higher proportion of macropores, which can be mitigated to resemble the curve shape of corresponding 24W series through subsequent water curing. Therefore, the variation in pore structure observed in the different SCMs pastes of 24SW can be seen as the process of optimizing the pore structure of 24S series to 24W series. Generally, the pore size distribution curves of all specimens separate three distinct regions with dividing lines around 10nm and 100nm. The curve shape is associated with characteristic changes influenced by the binder types, curing methods, curing duration. A notable phenomenon that all specimens show the peak within pore size of 100nm, which has been observed in many other standard-cured cement pastes and concretes (Cook and Hover, 1999; Cui and Cahyadi, 2001; Atahan et al., 2009). It indicates that the peak within the range of 100nm may be common to the cement-based matrix, while the majority of the pore distribution in the macropore region is likely attributed to the steam-curing process.

In order to compare the effect of subsequent water curing on the pore redistribution of each specimen for 24S series to 24SW series, Figure 2.13 is prepared for showing the percentage of the composition of three width intervals to its total porosity. The

macroporosity of concrete under S curing for 24N, 24FA, 24SG, and 24CA is 51.9%, 47.0%, 43.3%, and 48.4%, respectively, whereas for the 24SW series, it is 37.1%, 34.5%, 32.2%, and 38.9%. This indicates that post-water curing is beneficial for reducing macroporosity and increasing mesoporosity. For pores with a size smaller than 100nm, the curve observed in the 24SW series exhibit an increase compared to 24S. Figure 2.13 shows increase of mesoporosity of 24NSW, 24FASW, 24SGSW and 24CASW at about 44.1%, 46.1%, 35.6%, and 41.6% from those of 24S series about 32.8%, 34.2%, 23.9%, and 33.8%, namely. The rate at the relative proportion of micropores in 24S and 24SW series hardly changes. Under the steam curing methods for 24N and 24CA series, the pore structure of concrete is nearly identical, indicating that the material CA2 has little influence on the early internal pore structure of concrete and is insensitive to post-water curing. Furthermore, in the same binder pastes that underwent water curing, the pore size distribution exhibits nearly identical peaks in the mesoscopic pore range. The same phenomenon has been observed in many other standard-cured cement pastes and concretes (Cook and Hover, 1999; Cui and Cahyadi, 2001; Atahan et al., 2009). The increase in macropores resulting from steam curing is a key aspect that needs to be addressed to improve the pore structure of steam-cured concrete. Subsequent water curing and the addition of supplementary cementitious materials (SCMs) are both effective solutions to deal with this issue.

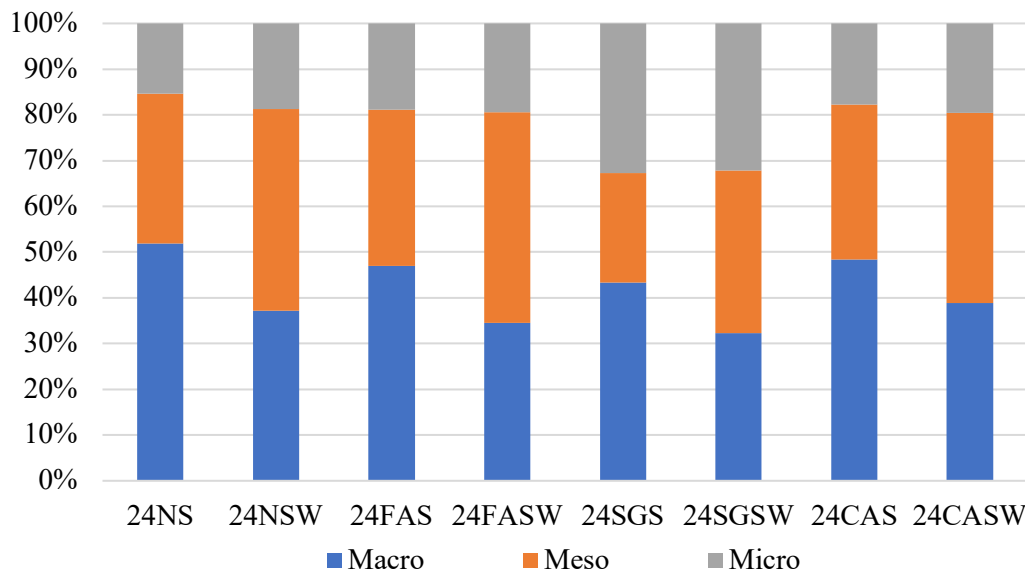


Figure 2.13 Self-comparison of porosity in three pore size intervals across four types of concrete in 24S and 24SW series

2.5.2 Mercury intrusion in normal-strength SCMs concrete after seawater exposure for one year

1) Pore structure of normal-strength SCMs concrete after one-year seawater exposure

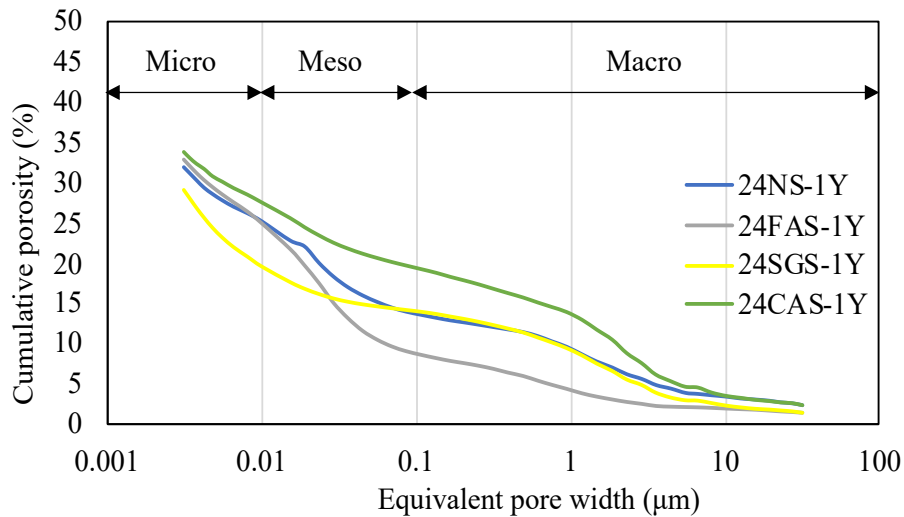
Steam-air cured specimens that had been subjected to one year of seawater immersion and placed in dry room, while the MIP test measured on 478 days. The abbreviation "-1Y" is added after the paste type to indicate the difference in curing time compared to specimens that were subjected to steam curing followed by air curing for 25 days, namely it is 24S series. The evolution of pore structure of steam-cured specimens in seawater is a focal point. Figure 2.14 provides the graphs of 24S-1Y series including the cumulative intrusion curve, pore size distribution curve and the specific porosities in three pore size intervals. Additionally, Figure 2.15 (a) to (d) presents the pore size distribution curves of the four concrete types: 24N, 24FA, 24SG, and 24CA, separately, for W, S, SW curing methods, and seawater exposure after one year (S-1Y).

The total porosity of the 24NS-1Y, 24FAS-1Y, 24CAS-1Y and 24SGS-1Y is around 29.7%, 31.3%, 30.8% and 27.5%, while the total porosity of four types of pastes remains similar values. The total porosity of 24S-1Y series has significantly decreased compared to the 24S series due to expose to seawater for one year, indicating that the cementitious materials in the 24S series underwent further hydration in the presence of seawater, especially in the specimens of fly ash and blast furnace slags. However, there was minimal change in the porosity of the 24CAS-1Y with that of the 24CAS. Further clarification regarding possible reasons could be obtained through a pore size distribution analysis.

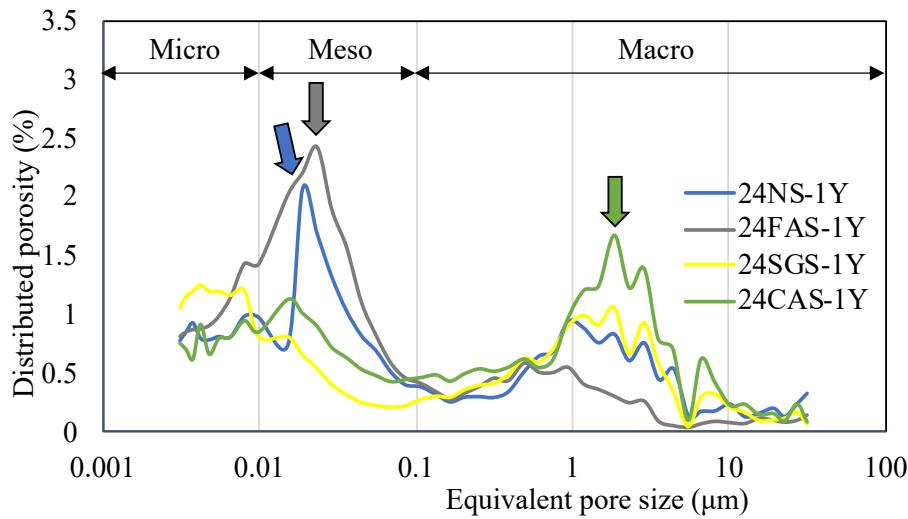
The pore size distribution curves (Figure 2.14(b)) of 24-1Y series generally can be divided into two zones in the pore size in 100nm that has not changed with that of 24S. In order to maintain consistency with the previous analysis of pore structure, it is advisable to divide the pore width of the 24S-1Y series into three zones using 10nm and 100nm as boundaries. The pore size intervals continue to be referred to as micropores, mesopores, and macropores. In the region where the pore width is greater than 100nm, the porosity of 24NS-1Y, 24FAS-1Y, 24SGS-1Y, and 24CAS-1Y is 11.3%, 7.16%, 12.5%, and 16.8% respectively. In the macropores range, the refining effect of fly ash cement paste is superior, whereas 24CAS-1Y exhibits nearly 1.5 times the porosity of 24NS-1Y (Figure 2.14). It is possible that the 24CAS-1Y has been affected by the ions in seawater, like sulfate ions. Sulfate ions in seawater can react with aluminum phase in the cementitious matrix to form potential expansive ettringite, a process known as sulfate attack, which may lead to cracks forming in pastes of 24CAS-1Y. This reason may provide an explanation for the lack of change in the total porosity of the 24CAS-1Y specimens before and after one year of exposure to seawater. It is possible that the formation of additional cracks has weakened the reparative effects on other pore widths. On the other hand, it may be referred that the metastable hydration products of CA2 can undergo mutual conversion, for example, the transformation of the hydration product of CAH₁₀ into the final form of C₃AH₆ results

in a 50% volume change (Scrivener et al., 1999; Bensted J, 2002). This process may lead to the formation of larger pores from the originally compact cementitious compounds. It indicates a potential reversal of pore structure evolution, characterized by a decrease in small pores and an increase in larger one. One more possibility is that these pores have evolved from the refinement of pores with widths larger than 31500nm. However, it has been previously discussed that SCMs have minimal refining effects on excessively large pores, making this possibility very unlikely. A constrained peak can be observed around a pore width of 1860nm in the curve of 24CAS-1Y, beneath which there are fluctuations in the curves of 24SGS-1Y and 24NS-1Y. Within a similar range of pore widths, the curve shape of 24SGS-1Y is very similar to that of 24NS-1Y. The curve distribution of 24FAS-1Y in the macropore region is the least pronounced, which is attributed to the pore size refinement caused by pozzolanic reaction. Furthermore, the pore distribution within the transition zone from macropores to mesopores, ranging from 100nm to 1000nm, appears to be barely impacted by the type of binder.

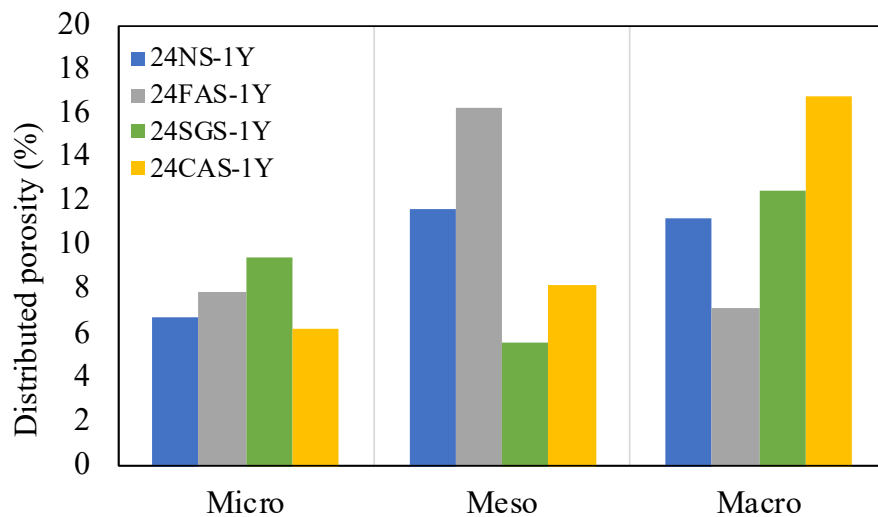
The mesoporosity for 24NS-1Y, 24FAS-1Y, 24CAS-1Y, and 24SGS-1Y were 11.7%, 16.3%, 5.60%, and 8.24%, respectively. The porosity curve for 24NS-1Y exhibited a distinctive peak around 20nm. A steep decline resembling a cliff-like drop was observed within the range of 20nm, which could indicate that mercury may have filled the open voids in this pore size. Assuming that the closed voids in the cement paste are relatively uniformly distributed within the matrix, the flat curve observed below size of 20nm may suggest that the mercury penetrated deeper into the uniformly distributed closed voids as the pressure increased, aligning with Cook's analysis (Cook & Hover, 1999). Notably, the mesoporous porosity of 24FAS-1Y reached 139.2% of that of 24NS-1Y. This substantial increase in porosity mainly originated from the transformation of macroscopic range, facilitated by the reaction of fly ash. A peak for 24FAS-1Y appeared around 25nm, with a gradual decline observed on the left side of the curve. This suggests that mercury continued to enter the connected smaller voids, indicating that this peak corresponds to the critical pore size. The porosity curve for 24SGS-1Y exhibited a continuous upward trend in the pore size between 10nm to 100nm. The porosity for 24SGS-1Y in this range was only 5.60%, indicating the significant refinement effect of the cementitious reaction facilitated by blast furnace slag on these pores. The porosity for 24CAS-1Y in mesoscopic range decreased dramatically compared to 24NS-1Y. This could be attributed to the fact that the hydration products of CA2 reacted with ions in seawater, further refining the pore structure within this width range to close voids. This could also result from the phase transition of initially voluminous CA2 hydration products, leading to the formation of voids within the compacted portion of the paste. Additionally, although the curve for 24CAS-1Y showed a slight convexity around 20nm, this width is evidently not the critical pore size compared to the larger pore widths above 1860nm. Furthermore, it appears that the curves for 24NS-1Y, 24FAS-1Y, and 24CAS-1Y all occurred a turning point within the 10nm-50nm width range, a shared characteristic observed in the 24W, 24S, and 24SW series. This common phenomenon may be attributed to the inherent properties of cement as a majority base material within this specific width interval.



(a) Cumulative intrusion curves of 24S-1Y series.



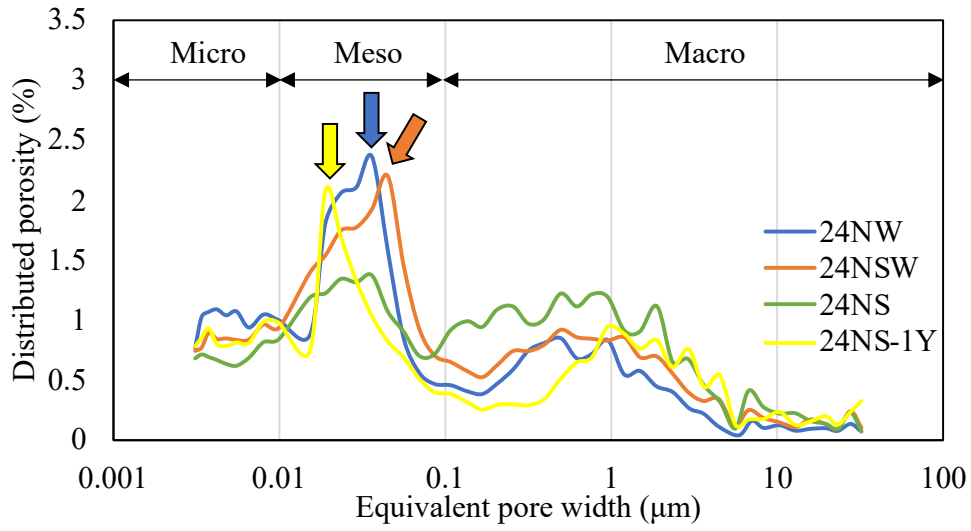
(b) Pore size distribution curves of 24S-1Y series



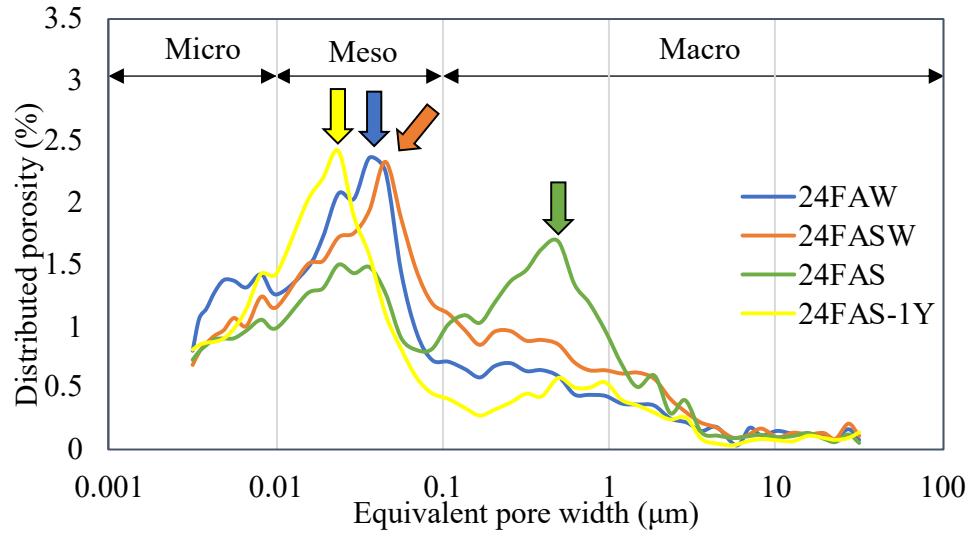
(c) Specific porosities in three pore size intervals of 24S-1Y series

Figure 2.14 Pore structure of four types of 24S series specimens after one-year seawater exposure (24S-1Y)

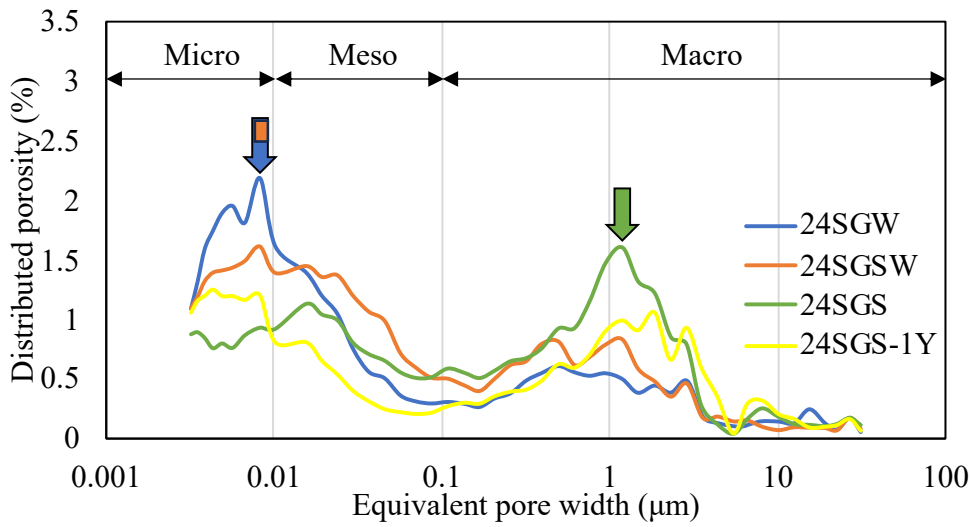
* Arrows marked in each color represent the critical pore size corresponding to the respective curve, with the data matching that in Table 4.



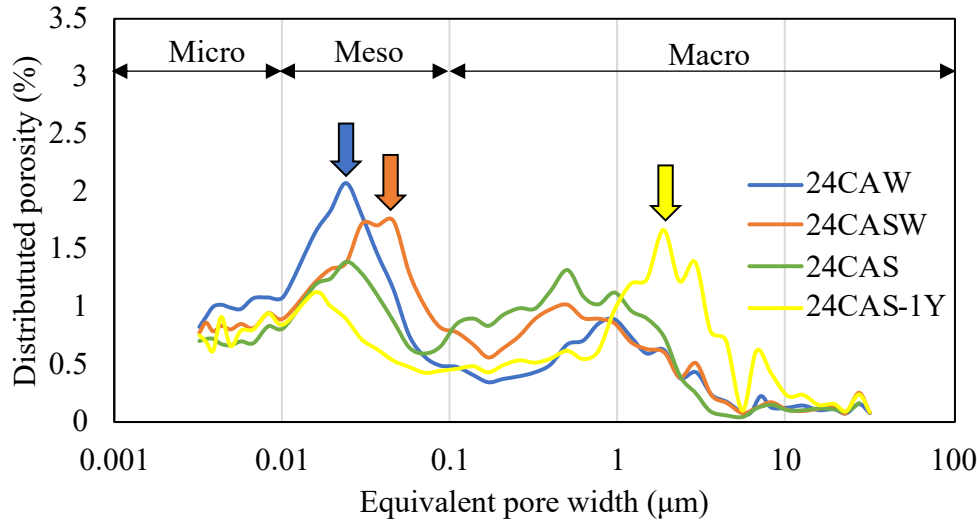
(a) Pore size distribution in 24N series



(b) Pore size distribution in 24FA series



(c) Pore size distribution in 24SG series



(d) Pore size distribution in 24CA series

Figure 2.15 Evolution of pore size distribution of 24 series under three curing methods during one-year seawater exposure

*Arrows marked in each color represent the critical pore size corresponding to the respective curve, with the data matching that in Table 4.

2) Pore structure evolution of steam cured SCMs cement paste in seawater for one year

The one-year seawater exposure clearly contributed to a denser pore structure for most of samples, with specific effects observed across different pore widths in Figure 2.15. Moreover, the evolution of the cumulative porosity curves indicates that the distribution of pores within the 24S-1Y series developed distinct characteristics associated with the binder. The distinctive effects of seawater exposure on different pore size intervals among four types of concrete can be examined, as Figure 2.15. The total porosity of the 24S-1Y series decreased from 27.5% to 31.3% to a range of 30.6% to 37.1% relative to that of 24S series. This analysis allows for a detailed assessment of changes in the distribution of pores across various size ranges, as shown in the Table 5.

2-1) 24NS series Vs 24NS-1Y series

The macroscopic porosity of 24NS-1Y is 60.4% of that of 24NS. The curve of 24NS-1Y exhibits a significant decrease compared to 24NS, particularly within the range of approximately 100nm to 1860nm, while the curves of the two samples overlap to some extent in wider pore width ranges. Furthermore, the curve of 24NS exhibits broader and rounded peaks, which convert into sharper and narrower peak distributions on either side of the pore width threshold at 100nm. Under seawater exposure periods the larger pores of the 24N series of cement paste might be filled, but its effect diminishes in larger pore ranges about 2000nm. Moreover, 24NS-1Y series appears that the rough impact of steam curing on macroscopic pores still exists after one year curing in relatively wider pore widths (>1000nm).

The pore width distribution curve of 24NS-1Y demonstrates that one year of seawater exposure allows for continuous hydration of the cement paste, resulting in densification

within the interior. However, when the capillary pore width reaches a certain level, the rough macroscopic pores distribution changes minimal, like the overlapping curves part of 24NS and 24NS-1Y. This may be attributed to a balance achieved through the continued generation of hydration products and the consumption of cementitious matrix resulting from multiple ion reactions in seawater.

2-2) 24FAS series Vs 24FAS-1Y series

During one year of seawater exposure, the macroscopic porosity of 24FAS decreased to 40.4% of that of 24FAS-1Y, representing the highest reduction among the four pastes, primarily attributed to the pozzolanic reaction. The peak in macroscopic range of 24FAS drastically decreased, which most likely converts to the porosity in mesopores. Within the mesopore range, the porosity of 24FAS-1Y is 126.1% that of 24FAS, with the critical pore size occurring at a pore width of approximately 25nm. The increased mesoporosity in 24FAS-1Y originates from the macroscopic pore range of 24FAS.

Both the dramatic reduction in macroscopic porosity and the increased mesoporous porosity benefit from the denser interior of the cement paste facilitated by fly ash. Steam-cured fly ash cement paste does not exhibit specific indications of roughness due to steam curing, as observed in 24NS-1Y at pore widths above 1800nm. It suggests that fly ash contributes to the refinement of the roughness associated with steam curing. Although the total porosity of 24FAS-1Y is relatively higher, the increased porosity is predominantly concentrated within the mesopores range, reaching 139.2% of 24NS-1Y, while the macroporosity is only 63.5% of 24NS-1Y. This indicates that fly ash has the ability to refine the pore structure of steam-cured cement paste in marine environments.

2-3) 24SGS series Vs 24SGS-1Y series

After one year of seawater exposure, the macroporosity of 24SGS-1Y decreased to 77.4% of that of 24SGS. As shown in Figure 2.15, the pore size distribution of 24SGS-1Y curve exhibited a significant decrease in porosity within the pore width range of 10nm to 1900nm. However, it seems that the pore structure of pore size above 1900nm has been preserved without distinct differences. Referring to the curve of 24SGSW, the 18-day water curing of steam-cured blast furnace slag cement paste has already demonstrated a refinement effect on the pore size distribution within the range of approximately 600nm to 2800nm.

Higher microporosity observed in the 24SGSW series compared to 24SGS-1Y does not necessarily indicate the generation of more hydration products during the 19-day curing period. Instead, it suggests that a significant number of finer voids in 24SGSW may have transformed into filled or closed voids over the course of one year of seawater exposure, which explains the minimal total porosity of 24SGS-1Y. This also indicates that, blast furnace slag cement paste is unlike the pore structure evolution observed in 24NS-1Y and 24FAS-1Y, which is possibly due to the high cement replacement rate of 50% with blast furnace slag.

2-4) 24CAS series Vs 24CAS-1Y series

It was known that the total porosity of 24CAS-1Y is only slightly decrease from 24CAS, with a difference of less than 1%. This difference is mainly due to the significant increase observed in the macropore region of 24CAS-1Y. Upon observing the curve shown in Figure 2.15, it can be seen that in the 100nm-1000nm range of 24CAS-1Y exhibits a significant refinement effect. However, 24CAS-1Y shows an increase in macroporosity in the pore size greater than 1000nm, and the critical pore size converts to about 1860nm. Moreover, the significant differences in pore distribution curves between 24CAS-1Y and 24NS-1Y may because the interaction between the CA2 hydration products in cementitious system and multiple ions in seawater may also influence the development of larger pores. The specific mechanisms underlying this phenomenon require further investigation and understanding.

According to the relative strength curves of 24CASW/24NSW in Figure 2.7, 24CASW series that underwent steam curing followed by water curing exhibited nearly identical strength to the 24NSW specimens until 91 days, after which a decrease of approximately 5% was observed, reaching around 10% at one year. It reveals that even in the absence of sulfate ions, the hydration products of CA2 may undergo phase transformations due to changes in curing time. These findings underscore the complex interactions between CA2 hydration products and environmental factors, such as curing conditions and exposure to seawater. Although the main purpose of CA2 material is for chemical binding of chloride ions in this research, the alteration in macropore voids did not result in a reduction of chloride resistance in 24CAS-1Y, as confirmed by subsequent chloride diffusion experiments. Further research is required to comprehensively understand the role of CA2 in influencing pore structure development over different hydration stages and under diverse environmental conditions.

Table 5 Increased/Decreased porosity in three pore size intervals after one year seawater exposure

	Pore size intervals		
	<10nm	10nm-100nm	>100nm
24NS-1Y/24NS	122.1%	99.0%	60.4%
24FAS-1Y/24FAS	110.8%	126.1%	40.4%
24SGS-1Y/24SGS	77.6%	63.0%	77.4%
24CAS-1Y/24CAS	109.7%	76.3%	108.7%

2.6 Chloride Penetration in Steam-cured SCMs Concrete

In this section, author conduct further investigation into the actual diffusion behavior of chloride ions in normal/high-strength steam-cured SCMs concrete under real marine conditions. It is worth noting that particular attention has been given to the CA2 material, whose function in concrete application shows promise in resisting chloride ion diffusion. Additionally, the chloride resistance of SCMs fly ash and blast furnace slag concrete subjected to three different curing methods in seawater also be examined. The detailed quantification of chloride diffusion behavior in all specimens is provided through chloride ion profiles using Silver Nitrate Extraction Procedure (JIS A 1154), while the approximate concrete chloride ion distribution images are obtained by Electron Probe Microanalysis (EPMA).

The concrete specimens under investigation were subjected to seawater exposure in Hokkaido for durations until one year. Chloride content measurements have been conducted three-time or above to confirm the accurate chloride content in the local part. The apparent chloride diffusion coefficients (D_c) were determined by the Fick's second law using the best fitting curve from MATLAB. The 24 series is consisted of normal-strength concrete with three different curing methods: standard curing (W), steam-air curing (S), and steam-water curing (SW). The 50 series consisted of high-strength concrete with a water-to-binder ratio of 0.34, which underwent two curing methods: standard curing (W) and steam-air curing (S). Chloride profiles of 24 series and 50 series for one year are listed in Figure 2.17 and Figure 2.19, and corresponding apparent chloride diffusion coefficients (D_c) are given in Table 6 and Table 9. Taking into account the potential influence of concrete surface quality on chloride ion penetration, chloride profiles were obtained from two different locations: the concrete casting surface (T) and the surface attached to the mold (B), and the representative D_c for the individual concrete applies the average values from both locations of the one sample. It's important to note that certain points of the chloride profile show anomalies. In such cases, these points are appropriately adjusted to meet the calculation conditions. Furthermore, a three-month exposure period is too short to present the concrete properties, thus the data in three months may not pay significant attention on discussing.

2.6.1 Chloride resistance of normal-strength SCMs concrete exposed to seawater for one year

EPMA and chloride ion content tests were conducted at exposure durations of 3-months, 6-months, and 1-year. The chloride profiles and the EPMA images of 24 series on three-month and six-month exposure to seawater are attached in Appendix A and Appendix B. The best fitting curves for all specimens are provided in Appendix C, where some specific data points were omitted from the analysis, and the rationale for such exclusions is detailed in the subsequent sections. In this section, EPMA has been utilized to understand the overall chloride ions distribution in concrete (Mori et al., 2006). While Hosokawa (2003), and Mori (2017), have suggested that EPMA can accurately estimate D_c , this does not hold true for many samples in this study, possibly

due to the complex composition of seawater and different sampling locations for EPMA and the conventional method for chloride test. The depth of chloride diffusion front identified through EPMA are presented on the fitting curves in Appendix C. Moreover, the spectral intensity in EPMA represents chloride ion concentration, ranging from 'bright white' to dark, indicating chloride ion concentrations from high to nearly 0. EPMA images were processed using ImageJ to distinguish the red spectrum, which typically represents chloride ion concentrations reaching 1.0% of the concrete mass. This parameter, along with the observed chloride diffusion front in EPMA, would be used in discussing various methods to limit chloride ion diffusion in SCM concrete later on. The depth of the red spectrum is labeled as "dh," while the overall chloride ion diffusion front is marked as "df", which are represented on the EPMA image as a dashed line and a solid line, respectively. Figure 2.16 presents EPMA images of the 24W and 24S series for one year, while three months and six months are depicted in Appendix D. In addition, the following sections frequently use abbreviations of specimen names, such as "24CAST" denotes the upper segment of normal-strength steam-air cured concrete incorporating CA2 additive.

1) Chloride profiles and apparent chloride diffusion coefficients in normal-strength SCMs concrete up to six-months seawater exposure

In the initial three months of immersion in seawater, a state of equilibrium characterized by diffusion as the predominant mechanism between the interior of concrete and seawater has not yet been established. Consequently, EPMA images in Appendix B show an elevated ingress of chloride ions into certain depth of the concrete, which could rely on various factors such as concrete saturation, ion concentration differentials, and ocean climate. However, it is important to note that this state of chloride ions within the concrete is not a permanent state. It might undergo changes as the concrete continues to densify within the seawater environment. The chloride profile and chloride diffusion coefficient (D_c) in Appendix A and Appendix C for the 24 series at three months and six months indicates chloride ion accumulation at the surface, whereas chloride ion seems to penetrate to deeper in the steam cured series possibly due to the rough pore structure and high saturation level in this concrete series, enabling chloride ions to infiltrate.

2) Chloride profiles and apparent chloride diffusion coefficients in normal-strength SCMs concrete after one year of seawater exposure

2-1) Chloride ions distribution in 24 series at one year via EPMA

EPMA images at one year are presented in Figure 2.16. Solid lines depict the visible chloride ion diffusion front, whereas dashed lines represent red spectral regions denoting areas with high chloride ion concentration, labeled as "dh" and "df" respectively. The experimental outcomes could be issues with experimental factors such as pixel size, X-ray intensity, and measurement time (Mori and Yamada, 2007). In EPMA images, standard-cured concretes appear that exposure to seawater between six months and one year seems to minimally impact the overall chloride diffusion,

particularly in the upper part. This finding implies that after being immersed in seawater for a year, concrete possesses sufficient strength to withstand the destabilizing effects caused by marine climate conditions. The confined chloride ion distribution in the upper part of 24CAW-1Y concrete might arise from errors or inherent unpredictability in concrete behavior.

The EPMA images obtained after one year for 24S series reveal a consistent trend of chloride ion penetrate into deeper concrete layers across all concrete types. Notably, certain steam-cured specimens exhibit abrasion near the surface, exposing aggregates, while this phenomenon in standard-cured specimens with the same binder is less pronounced. The deterioration of concrete surfaces in 24S specimens is potentially aiding continued chloride penetration. EPMA images reveal well-controlled chloride ion penetration depths for one year in steam-cured concrete containing CA2 with a shorter chloride diffusion front compared to the standard-cured group. The chloride diffusion front in 24SGS-1Y concrete also remains restrained due to steam curing. This may be attributed to that steam cured CA2 material enhanced chloride ion binding capacity and competitive ion diffusion within the concrete matrix. On the other hand, the presence of a deeper chloride front in 24FAS-1Y could be linked to a negative effect of low temperature of seawater, limiting hydration of fly ash until one year.

In the case of 24NW, the parameter of df is consistently smaller than that of 24NS for one year exposure due to the rough internal structure caused by steam curing. However, the similarity between the chloride ion diffusion front of 24NS-1Y and 24NW-1Y suggests that the primary impact of steam curing is increasing the depth of a larger amount of chloride ion penetration. The considerable discrepancy in both ' df ' and ' dh ' between 24FAS and 24FAW emphasizes the lasting influence of steam curing, which results in a coarser pore structure allowing ion ingress into the interior of 24FAS. Additionally, the compensatory effects of the temperature-sensitive pozzolanic reaction of fly ash are absent in cold seawater. This outcome highlights the necessity of considering temperature-induced implications for the practical application of normal-strength steam-cured fly ash concrete in real environments. However, in this study, no issues like 24FAS-1Y were observed with steam-cured blast furnace slag concrete. EPMA images of blast furnace slag concrete demonstrate its high-performance resistance to chloride ion diffusion, unaffected by the curing method. Besides, the ' df ' in 24SG concrete at one year is nearly half that of the control group (24N series). However, 24SGS demonstrates more significant capacity to limit the ' dh ' and ' df ' to the control group than that of the 24SGW series. Conversely, the EPMA images and Table 7 of 24CAS shows a slightly escalated ability than 24CAW on restricting the transport of chloride ions. Furthermore, the concrete quality of both the upper and lower parts of 24CAS exhibits a greater stable ability against chloride diffusion compared to 24CAW and 24CASW. The higher level of controllable concrete quality is a notable advantage for practical engineering applications, which means that the normal-strength steam-air-cured CA concrete is appreciable. On the other hand, the observation of chloride ion accumulation in areas surrounding coarse aggregates suggests that larger aggregates might hinder the chloride penetration into the deeper layers of concrete.

2-2) Chloride profiles and corresponding Dc of 24 series at one year

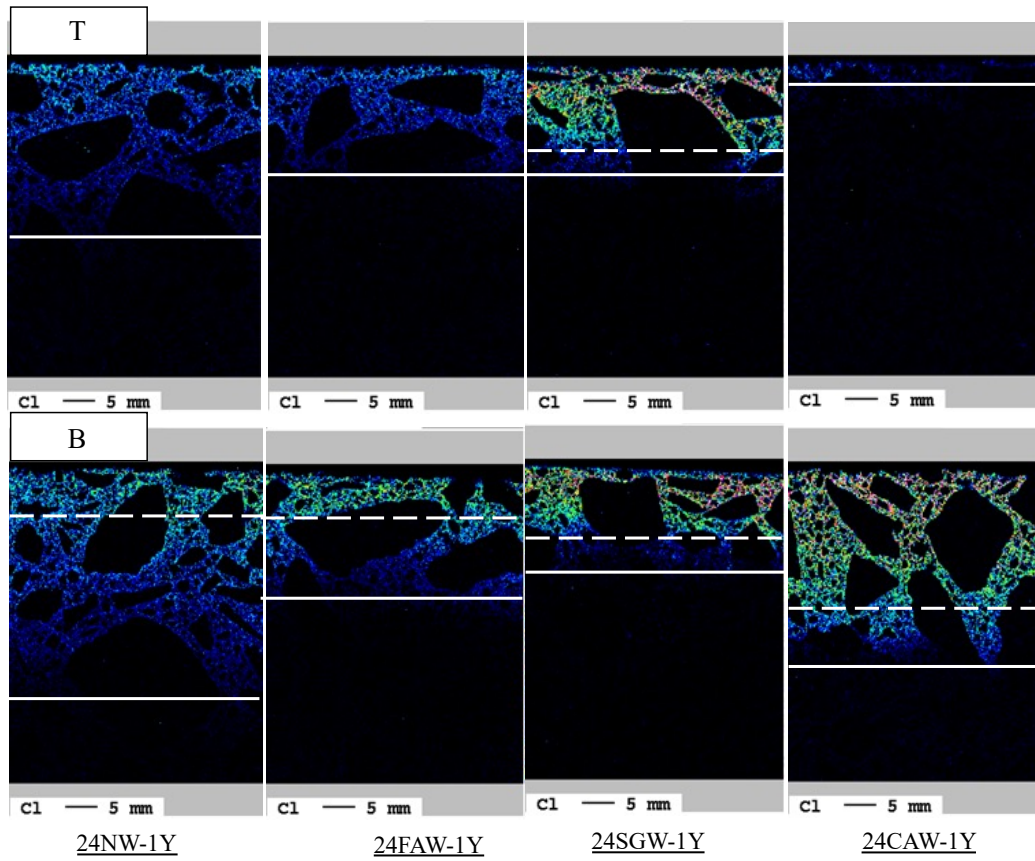
At the one-year mark, the upper and lower chloride profile of standard-cured concrete displays notable different, as shown in Figure 2.17(a). The variation appears at varying depths from the surface, with lower chloride content in the upper part of concrete and a higher chloride distribution in the lower part of concrete, regardless of concrete type. This indicates potential quality differences of normal strength standard-cured concrete between upper and lower portions due to the initial curing stages. It's advisable to analyze chloride profiles of standard-cured specimens, distinguishing upper and lower sections. Among upper part of specimens, 24NWT-1Y exhibits highest chloride diffusion in deeper concrete. 24FAWT-1Y, 24CAWT-1Y, and 24SGWT-1Y show similar chloride ion levels, while elevated concentrations in slag-blended concrete surface layer maybe due to salt accumulation around the large void near to concrete surface. Lower concrete part of chloride profiles shows diverse chloride profiles based on binder type. Blast furnace slag concrete has lowest concentration at each layer, followed by fly ash, and then CA concrete. 24NW-1Y has higher chloride ion content in deeper layers with a deeper chloride front, aligning with EPMA image findings. After one-year seawater exposure, an uneven distribution of chloride ions is observed in standard-cured concrete, extending from both surfaces inward. During the concrete setting process, large aggregates may settle due to gravitational effects, leading to a slightly uneven distribution of paste and aggregates, especially for specimens with longer initial setting times. It is well known that chloride ions primarily transport within interconnected pore system of concrete, where the cementitious matrix is the main contributor for capillary porosity. According to this theory, there should have been a higher chloride concentration in the concrete of the cast layer, which contradicts the findings observed in this study at 24W-1Y series. Therefore, the effects of less gel-like hydration products to refine in local concrete parts and coarser ITZ must not be overlooked. Low-temperature environments may elevate stress exerted on pore system could result in thermal crack formation due to inadequate cementitious products support, allowing chloride ions to ingress into the concrete by multiple ways. Additionally, the stress of salt accumulation in pore wall and calcium leaching could lead to concrete weak to facilitate chloride diffusion. These factors could contribute to the varying chloride diffusion levels between the upper and lower part of the 24W concrete. Nevertheless, SCMs in concrete consistently demonstrate enhanced resistance against chloride diffusion in concrete compared to 24N-1Y series under any curing method. The additional hydration products from fly ash and blast furnace slag helps fill into concrete pore structure and immobilizes chloride ions to form solid products to restrict free chloride transportation in concrete. In the case of 24CAW-1Y, the chloride profile consistently exhibits lower values compared to 24NW-1Y, except for the outermost layer near the concrete surface. Additionally, its chloride ion diffusion front is noticeably shallower than that of 24NW-1Y. The Dc ratio of 24CAW-1Y and 24NW-1Y is 0.45, while the comparative values of Dc for other SCM concretes can be found in Table 8. It indicates that the CA2 additive exerts effective ability on limiting chloride diffusion in standard-curd concrete.

The chloride profiles of steam-air-cured concrete in Figure 2.17(b) exhibit greater complexity at the one-year interval compared to four types of standard-cured concrete. Symmetry in chloride ion concentrations on upper and lower surfaces of the same concrete type suggests steam curing may address issues during standard curing's setting time. 24FAS-1Y's chloride profile aligns with or exceeds that of 24NS-1Y in deeper regions. This phenomenon could arise from the delayed and less pronounced contribution of fly ash reaction in enhancing chloride resistance until one year. EPMA images also demonstrate the temporal evolution of chloride ion distribution in the 24FAS series, revealing a process where chloride ions first diffuse to greater depths at very low concentrations before gradually accumulating to form a concentration gradient. Furthermore, the low-temperature sweater curing may postpone the fly ash hydration. Therefore, the Dc value of 24FAS-1Y is the highest among the tested curing methods. The sharp decline in the chloride profile curves of 24CAS-1Y signifies a rapid decrease in chloride ion content with a deeper depth. This phenomenon aligns with the short 'd*' provided by the EPMA image of 24CAS-1Y. Prior to this, the chloride profile of 24CAS-1Y was closer to and slightly higher than that of 24NS-1Y. Based on the MIP result, a mere 7% cement replacement rate with CA2 material did not lead to denser in the pore structure of the concrete. The high chloride ion binding capacity of CA2 hydration products can account for all the aforementioned phenomena: the shallower chloride diffusion front compared to 24NS-1Y is due to chloride ions being immobilized within a specific region, while the slightly higher chloride concentrations in different layers to 24NS-1Y result from chloride ion accumulation. Thanks to the contribution of CA2 additive, the average Dc for 24CAS-1Y is 0.53 times that of the control group at one year. It implies that the robust chloride resistance of CA2 has not been compromised by the increased porosity at macro-range. That is, in Section 2.5.2, the increased macroporosity in 24CAS-1Y is more likely due to a phase transition. In cementitious systems, the product of calcium aluminate compounds undergoing sulfate attack is ettringite, which does not limit chloride ion penetration capability. Steam-cured concrete incorporating with blast furnace slags proves to be more effective to reduce the chloride penetration after the one-year seawater exposure experiment, which Dc is only 0.30 times of 24NS-1Y.

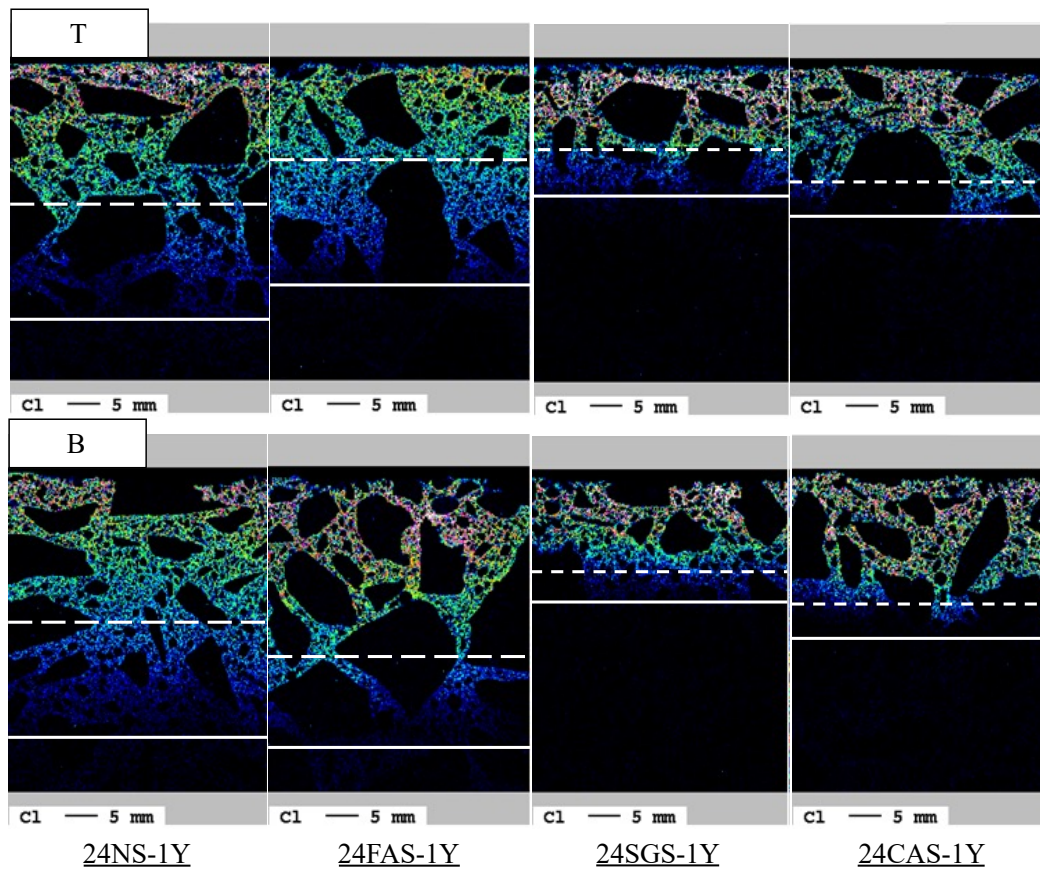
Figure 2.17(c) illustrates the chloride ion distribution in 24SW-1Y specimens. The profile of 24NSW-1Y and 24NS-1Y overlap considerably, suggesting diminishing differences between steam-air curing and steam-water curing over one year of exposure. In 24FASW-1Y, shallow depths have higher chloride ion content than 24NSW-1Y, but the trend reverses in deeper layers with observed chloride ion diffusion front. Lower chloride ion content in the deeper part of 24FASW-1Y suggests that the pozzolanic reaction has had playing a role on hindering chloride diffusion. In general, adequate moisture availability after steam curing can enhance chloride resistance in steam-cured fly ash concrete in long-term compared with 24FAS-1Y. Furthermore, warmer seawater during August to November contributes to accelerate the pozzolanic reaction. However, a chloride accumulation in outer layers of 24FASW-1Y, and a similar situation also occurs on the top surface of steam-cured blast furnace slag concrete. It could be

attributed to surface degradation that occurs after a period of seawater exposure for steam cured SCM concrete. It might be due to ion exchange between the solid components of concrete and seawater, and there could also be a possibility of salt spalling, especially considering the low winter seawater temperatures in Hokkaido. The chloride ion curve of blast furnace slag concrete at one year exhibits a rapid reduction in chloride content with increasing depth, irrespective of the curing method employed, indicating a generally superior chloride resistance.

Despite the decreasing D_c for 24N and 24CA concrete in both the 24S-1Y and 24SW-1Y series as the exposure time to seawater up to one year, the D_c values of specimens under the former curing method is lower. Before discussing this phenomenon, it's essential to clarify that the transport of chloride ions in concrete relies on pore solution as a medium. If the concrete is too "dry" or the saturation of pore solution is too low, the mass transport of chloride ions becomes challenging. EPMA images of ultra-high-strength concrete as presented by Mori (2017) also indicate trace amounts of chloride ions in specimens subjected to water curing, whereas those under dry curing show none. In terms of 24NSW and 24CASW, they could have had relatively high saturation levels in pore system before exposure to seawater, which may allow excessive amount of chloride ions to ingress along the wet interconnected pore system. This idea could also explain the high chloride ion concentration observed in the deeper layers of 24SW series after three months of seawater exposure. On the other hand, MIP experiments revealed that the pore structure of 24SW series of N and CA concrete was slightly finer compared to 24S before immersion in seawater. However, the higher amount of chloride ions penetrates into 24SW series, indicating that the concrete structure had not yet become compact enough by post-water curing to impede chloride penetration. As a result, the D_c values for the 24NSW-1Y and 24CASW-1Y remain higher than steam-air curing methods. Nonetheless, the difference of profiles between 24S series and 24SW series diminishes with increasing duration of seawater exposure. Furthermore, the concrete in the 24S series was exposed to warmer seawater conditions for an additional two months to 24SW series, from six months to one year in exposure duration, which could also account for differing effects on chloride penetration and concrete hydration between the two concrete types. Additionally, a careful examination of the chloride profiles in 24CA and 24N reveals that the chloride distribution in the shallow layers of CA concrete closely resembles that of the N series, with slightly higher levels. This might be due to the enhanced binding of chloride ions by CA2 hydrations, contributing to the overall chloride content without causing harm. However, 24FAS exhibits the relatively poorest performance among the fly ash concrete series in three curing methods. This may be explained by that fly ash hydration is sensitive of water supply. According to above experiment results of the normal-strength SCM concretes, steam-cured fly ash concrete benefits from sufficient subsequent water supply, while CA concrete is suitable for steam-air curing, and blast furnace slag with a 50% cement replacement rate is suitable for all curing methods considered in this study.

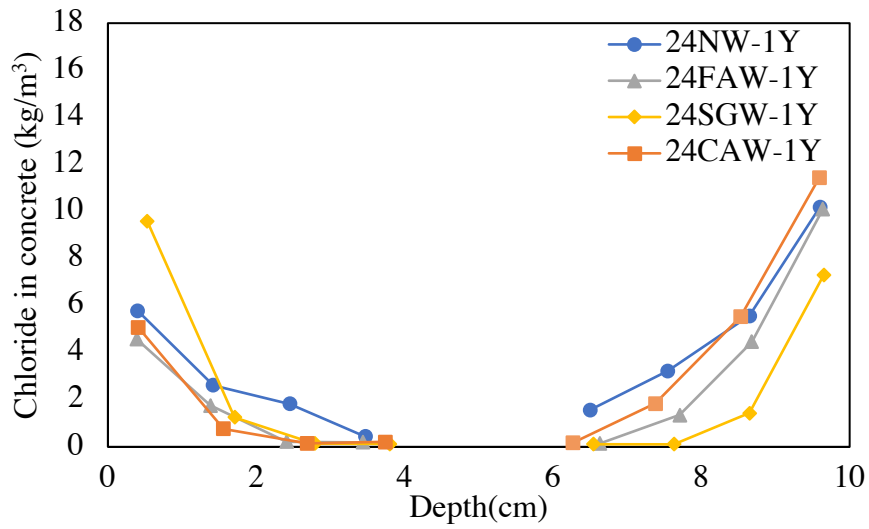


(a) EPMA images of 24W-1Y series

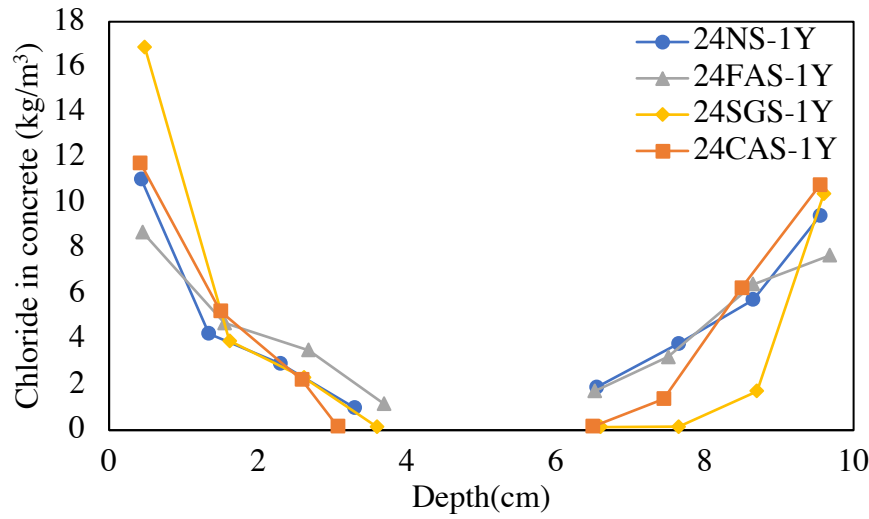


(b) EPMA images of 24S-1Y series

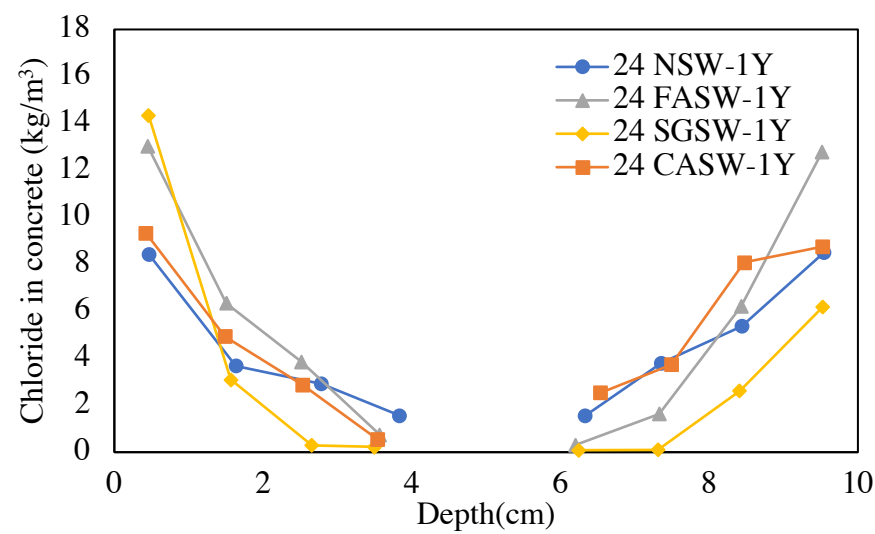
Figure 2.16 EPMA images of (a) 24W-1Y series and (b) 24S-1Y series



(a) Chloride profile of 24W series



(b) Chloride profile of 24S series



(c) Chloride profile of 24SW series

Figure 2.17 Chloride profiles of 24 series under three curing methods for one-year seawater exposure: (a) the standard-cured concretes (b) the steam-air-cured concretes

Table 6 Apparent chloride diffusion coefficient (D_c) of 24 series concrete

Dc of 24 series at one year (cm^2/year)			
	W-1Y	S-1Y	SW-1Y
24NT	1.86	1.44	3.04
24NB	2.36	2.68	3.91
24N ave	2.11	2.06	3.47
24FAT	0.82	3.17	1.91
24FAB	1.01	2.85	1.45
24FA ave	0.91	3.01	1.68
24SGT	0.47	0.86	0.58
24SGB	0.46	0.39	1.07
24SG ave	0.47	0.63	0.82
24CAT	0.46	1.33	2.09
24CAB	1.46	0.83	2.61
24CA ave	0.96	1.08	2.35

2.6.2 Effect of binder types and curing methods on chloride penetration in normal-strength steam-cured SCM concrete in marine environment

1) Influence of binder types on D_c in 24 series

In order to highlight the variations in D_c over time among different types of binders, Table 8 presents the ratio of the D_c values between the SCM concrete and N series under the same curing method. The term "Dc ratio" in the subsequent discussion refers to the meaning above. It's worth noting that when concrete is exposed to seawater for a relatively short duration, the interaction between the concrete and seawater may not reach a stable state, making a 3-month and 6-month interval comparison impractical. Therefore, the comparison of D_c before one year is not included in later context.

For fly ash concrete, specimens that underwent water curing before the seawater exposure experiment, such as 24FAW and 24FASW, displayed that D_c ratio were less than 0.5 after one year of exposure, but D_c of 24FAS exhibited 1.46 times of 24NS series. It's important to note that 24FASW has been exposed to seawater since August. These findings underscore the specific requirements for fly ash concrete that an adequate moisture curing and curing temperature is appreciable. In contrast, the chloride resistance of slag concrete remains unaffected by curing methods and exposure duration. The D_c ratios of 24SG/24N are significantly lower, indicating that the 50% cement mass replacement with blast furnace slag results in concrete that can consistently provide an excellent efficient to counteract chloride diffusion. Both 24CAS and 24CASW show a low D_c compared to respective 24N series. It implies that MIP results indicate that increased macroscopic porosity in steam cured CA concrete had no negative influence on the D_c . Steam-air-cured CAS demonstrates that even without post-water curing, CA concrete can offer excellent chloride resistance, presenting a highly valuable commercial advantage. Currently, a long-term investigation into chloride resistance in CA concrete is urgent.

2) Development of Dc in the 24 series over one year of seawater exposure

Development of Dc in four types of concrete over one-year seawater exposure, it needs to reference data from Appendix D, detailing the Dc of the 24 series and the Dc ratio of 24SCM/24N series at three and six months, along with the one-year data in Table 6 and Table 8. All specimens exposed to seawater reduced Dc values over time, which is mainly due to ongoing hydration processes in seawater, densifying the internal structure. In the study, some specimens did not exhibit a consistent decrease in Dc over the one-year period, prompting consideration of the impact of seasonal variations in seawater temperature on chloride diffusion behavior. Varied degrees of Dc reduction indicate distinct supplementary cementitious material impacts on developing chloride resistance. Among steam-cured concretes, significant Dc changes over time are seen in 24FA series, with outcomes influenced by subsequent water curing before the seawater exposure and seawater temperature. The significant discrepancy in chloride resistance among fly ash concretes under different curing methods indicates their high sensitivity to environmental factors. Moreover, a relative stable chloride resistance is observed in 24CA and 24SG concretes, especially in steam curing series. Steam-cured blast furnace slag concrete exhibits lower strength at 14 days, 28 days, and 91 days due to extended hydration time required by blast furnace slag. Moreover, seawater's complex ion composition stimulates dense hydration product formation and immobilizes free chloride ions within the slag (Li et al., 2018). CA concrete yields results comparable to SG concrete, emphasizing its crucial chemical role. Therefore, the Dc of 24CA series remains significantly lower than 24N series, regardless of time interval.

3) Performance of SCMs concrete in cold-region seawater

It has been confirmed that fly ash and blast furnace slag are effective in enhancing the resistance of concrete against the penetration of chloride ions in marine environments. Typically, the mechanisms underlying the effects of these two supplementary cementitious materials are more inclined towards physically densifying the concrete matrix, with some contribution from chemically fixing chloride ions primarily due to the presence of aluminum phases within the materials. However, in this study, steam cured concretes as well as standard cured concretes with SCMs were immersed from the end of October in natural seawater with minimum temperatures around 1.5 Degree Celsius in mid-winter periods. Then, the hydration and chemical reactions in the concretes within early exposure periods were limited. This severe condition would have influence on the chloride penetration. Moreover, the significant chloride diffusion inhibition ability of the 24CA concrete series is apparent in the chloride profile analysis, with its primary efficacy lying in chloride ion immobilization (Tabara et al., 2010 and 2013). However, the varying dominant capacities to restrict chloride diffusion among concrete types may find expression in the EPMA images. The width of the gradient concentration between high and low-concentration areas of chloride ions varies based on the type of concrete. Mori (2017) mentioned about the “wall effect” from Yamada’s research that EPMA images of ultra-high strength concretes exhibit a phenomenon, in which concrete keeps chloride ions in regions, acting like a "wall," obstructing chloride

ions from diffusing into the interior of the concrete. Similar behavior has been observed in 24SGS-1Y and 24CAS-1Y concrete investigated in this study.

One of the significances of this study is the investigation of chloride resistance in steam-cured CA concrete. Although previous research has stated a trend of reduced chloride diffusion depth in CA concrete (Ito et al., 2018, Miyawaki et al., 2021), the author believes that relying solely on diffusion depth does not provide a comprehensive representation of the restrictions imposed on chloride ions within CA concrete. Therefore, this study employs EPMA imaging, processed through software, to delineate regions where chloride ion concentrations reach 1% of the concrete's mass. Contrasting this region with the visually observable chloride ion diffusion depth provides a more intuitive representation of the limitations on chloride ions in SCM-enhanced concrete. According to the EPMA images in Figure 2.16 and the images in Appendix B, those are evident that the distance between the dashed and solid lines, which represents the boundary from the concrete surface to the high chloride ion concentration region is denoted as "dh", while the overall chloride ion diffusion front is referred to as "df", and the distance between these two points is simplified as "d*". A summarized data at one year is provided in Table 7, while the three-month and six-month data as shown in Appendix B. In general, the boundary of high chloride concentration region is located to the chloride diffusion front less than 1cm for the 24CA and 24SG series, irrespective of curing methods. In contrast, for 24N and 24FA, the minimum gap distance is 1.2cm, and it can even reach up to 3.6cm depending on the curing method. In the case of 24NW, the depth of chloride diffusion front is consistently smaller than that of 24NS due to the rough internal structure caused by steam curing, while the opposite shows in dh. It indicates that chloride ions penetration in 24NS is deeper and in larger quantities into the interior, aligning with the trend observed in the chloride profiles. The blast furnace slag concrete shows a consistently short low-chloride ion area throughout, possibly attributed to its dense internal structure and chemical binding capacity. On the other hand, the chloride ion distribution pattern of CA concrete shows similar to that of blast furnace slag concrete. However, whether assessed through MIP or strength development, the performance of CA concrete closely resembles that of the control group, as CA2 replacement is only 7%. Additionally, the hydration products of CA2 do not yield significant gel-like formations, which means that the hydration products of CA2 cannot provide notable refining effects for concrete. Consequently, the shorter depth of chloride diffusion front of CA concrete can be attributed to its strong chemical binding capacity for chloride ions. In other words, CA concrete, owing to its strong chemical binding of chloride ions, effectively seizes and hinders the diffusion of chloride ions into the concrete interior. However, when the quantity or diffusion rate of chloride ions exceeds the limitation capacity of the partial CA concrete, chloride ions may continue to penetrate deeper. Still, chloride ions are firmly constrained upon encountering new CA2 hydration product interfaces. This may explain why "d*" remains constant for 24CAS. If the discussed diffusion mechanism in CA concrete holds reliability, it suggests that when the chloride ions front in CA concrete reaches the depth of the rebars, the loss of chloride ion resistance in the concrete protective

layer is not far away. A high-density inner structure of 24SG concrete may primarily act as a barrier, preventing chloride ions from entering. The chloride distribution observed in 24FAS concrete, unlike the previously researched efficient limitation of chloride diffusion, indicates that fly ash concrete is more sensitive to actual exposure environments. This constitutes a novel discovery from this research. In future work, for precisely understanding this diffusion behavior in concrete that requires extra attention to chloride ion chemical binding capacity, more data collection is needed.

Table 7 Depth of high-concentration chloride region and overall chloride diffusion front in EPMA images of 24 series concrete

Depths of the high chloride concentration region and the chloride diffusion front (cm)									
		24W				24S			
		N	FA	SG	CA	N	FA	SG	CA
T	1Yh	-	-	1.4	-	2.1	1.5	1.4	-
	1Yf	2.3	1.7	1.7	0.4	3.8	3.2	1.7	0.4
	1Y*	2.3	1.7	0.4	0.4	1.7	1.7	0.4	0.4
B	1Yh	0.7	0.7	1.1	2.2	2.2	2.6	1.1	2.2
	1Yf	3.6	2.0	1.6	3.1	3.8	3.9	1.6	3.1
	1Y*	2.9	1.3	0.5	0.9	1.7	1.3	0.5	0.9

The high-concentration region and the diffusion front of chloride ion in EPMA images have marked on EPMA images, in which depth are denoted with suffixes "h" and "f," respectively, while the "" represents the distance from the boundary of the high-concentration region to the part free of chloride (unit: cm).

Table 8 Dc ratio of 24SCM series compared to the respective N series under three curing methods after one-year seawater exposure

Dc ratio of 24SCM/24N			
	24W-1Y	24S-1Y	24SW-1Y
FA/N	0.43	1.46	0.48
SG/N	0.22	0.31	0.24
CA/N	0.45	0.53	0.68

4) Correlation of Dc and pore structure in steam cured SCMs concrete

The transportation of chloride ions in concrete is primarily influenced by the pore system within the cementitious matrix, particularly the interconnected pores. According to Hashimoto (2010), the depressurization curve from MIP can to some extent represent the geometrically connected pore structure within the cementitious matrix. A distinctive correlation between specific pore widths and Dc was identified by analyzing MIP data obtained during the decompression of all series, along with corresponding time-period Dc measurements. The x-axis represents the porosity corresponding to the depressurized mercury volume between a specific pore width, while the y-axis corresponds to the Dc of the 24S-1Y series concrete. As illustrated in Figure 2.18, there is a positive correlation between Dc and the decompression porosity within the pore width range of 100nm to 2100nm. Moreover, a negative relationship between Dc and the depressurized porosity within the pore width range of 3800nm to 5200nm is observed. It is known that chloride ion movement within concrete is most facile in highly connected pore structures. This suggests that the pore connectivity within the 100nm to 2100nm range of specimens subjected to one year of steam curing might be relatively high. On the other hand, larger pores exceeding 3800nm might represent isolated pores. If these pores constitute a significant proportion of the total, it implies that the contribution of highly connected pores could be relatively limited.

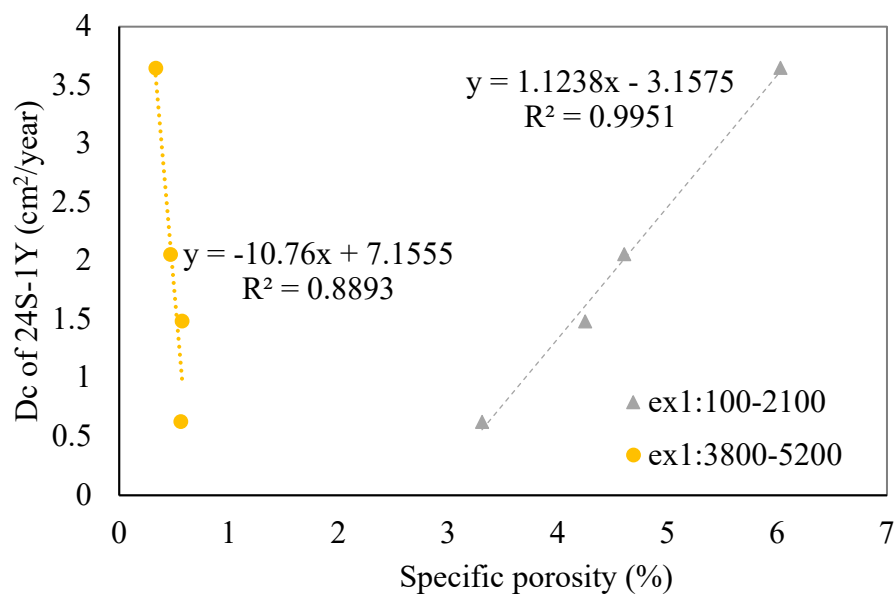


Figure 2.18 Relationship of Dc and depressurization porosity of the 24S-1Y series

2.6.3 Chloride penetration in high-strength SCMs concrete exposed to seawater for one year

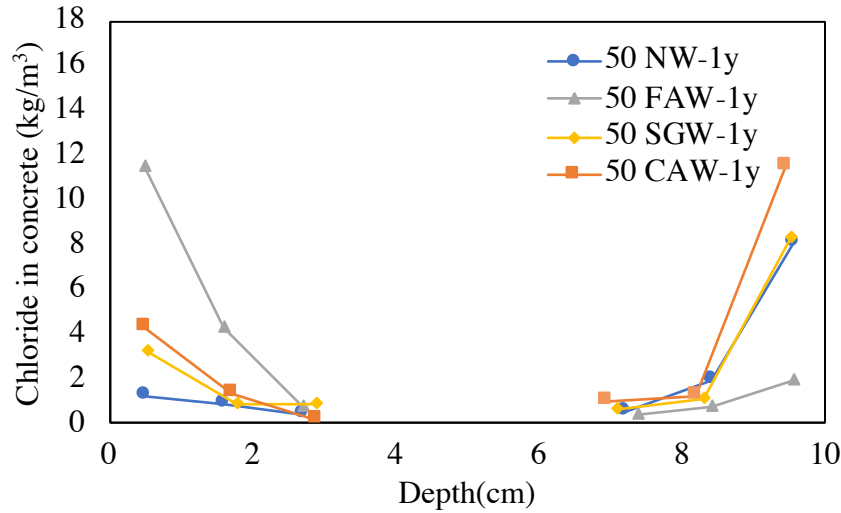
1) Chloride profiles and Dc of 50 series at one year

Figure 2.19 presents the chloride profiles for the 50W and 50S concrete series at one year, with graphs and Dc for three and six months available in Appendix A and Appendix D. The 50W series concrete exhibits a subtle indication of inward diffusion into the depth of the concrete with the prolonged duration of immersion in seawater. Moreover, chloride profiles for one year indicate that the chloride ion distribution of steam-cured concrete is almost consistent in any binder type, signifying that a low binder water ratio is one factor dominant over SCM type on the chloride resistance of concrete. Table 9 displays Dc of 50W series and 50S series concrete at one year, where the chloride distribution of some abnormal points has been removed from calculation of Dc, such as the surface layer of the concrete of 50NWT-1Y, and 50FAWB-1Y and 50SGWT-1Y. 50NW-1Y, 50FAW-1Y and 50SGWT-1Y within the 50W-1Y exhibit extremely low chloride ion content in the concrete surface layer. This suggests that one year of seawater exposure may not lead to chloride diffusion in high-strength standard-cured concrete, potentially resulting in errors in calculated Dc values. It implies that high-strength concrete will take a longer time to build diffusion behavior when reaching equilibrium with seawater. Therefore, in such instances, the Dc applies to the value of the other half part of the concrete. In general, the Dc values for steam-cured specimens are lower than those for specimens subjected to standard curing for the same type of binder and testing duration although longer exposure period than one year may result differently. This phenomenon may result from the steam curing process in the 50S series, which creates a coarser pore structure, allowing for certain chloride ion penetration paths. Thus, the calculated chloride diffusion coefficient of 50S series, based on Fick's second law, yield relatively reasonable low chloride diffusion coefficients. Another potential reason is that for the 50 series concrete, one-year exposure in seawater might not establish a concentration gradient meeting chloride diffusion behavior. Therefore, the calculation of Dc might not accurately represent the high-strength concrete's actual resistance to chloride ions. It means that high-strength concrete may require a longer experimental durations in salt environment. This anticipation might find fulfillment in Chapter 3, where the high-strength steam-cured SCM undergoes a chloride penetration experiment for up to three years.

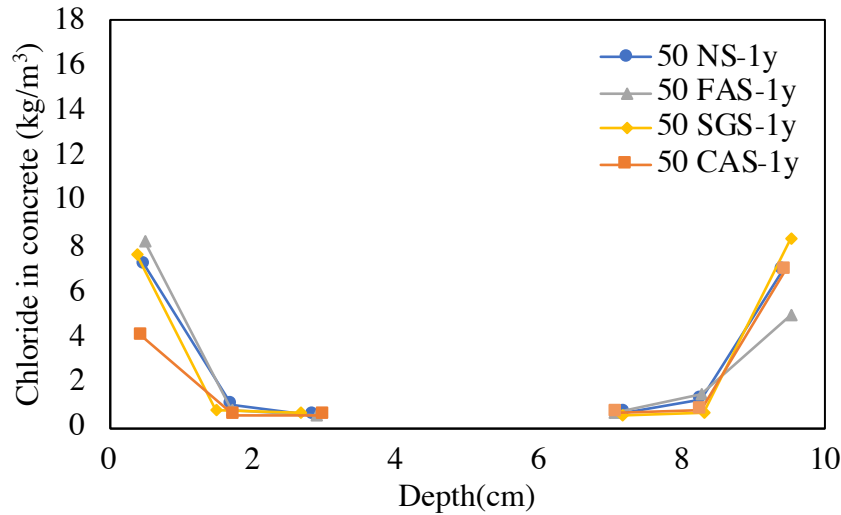
Table 9 Apparent chloride diffusion coefficient (Dc) of 50 series concrete

	Chloride diffusion coefficient of 50W and 50S series (cm ² /year)							
	NW-1Y	FAW-1Y	SGW-1Y	CAW-1Y	NS-1Y	FAS-1Y	SGS-1Y	CAS-1Y
T	3.45*	1.02	0.49	0.99	0.52	0.40	0.33	0.66
B	0.68	2.32*	0.49	0.46	0.63	1.22	0.38	0.49
Ave	0.68	1.02	0.49	0.73	0.57	0.81	0.36	0.58

*Chloride ion content in the surface concrete of 50NWT-1Y and 50FAWB-1Y is excessively low, potentially leading to significant calculation errors.



(a) Chloride profile of 50W series at one year



(b) Chloride profile of 50S series at one year

Figure 2.19 Chloride profiles of 50 series under (a) standard curing and (b) steam-air curing over one year

2) Influence of binder types on Dc in 50W and 50S series

By examining Dc ratio between SCM and N series under the two curing conditions, insights into the hydration behavior of different additives on contribution to the resistance to chloride penetration. Based on the one-year seawater exposure experiment data, both 50FAW/50NW and 50FAS/50NS exhibit Dc ratios exceeding 1. It needs to account for temperature fluctuations during the seawater exposure period. Concrete specimens within the 50 series were introduced to seawater at the end of June, undergoing the six-month to one-year seawater exposure period encompasses the colder temperatures of winter and spring, potentially affecting the hydration of fly ash, which is sensitive to environmental temperature and might be influenced more significantly than cement particles. Additionally, some 50 series specimens present surface chloride ion concentrations that result in Dc errors, suggesting that a one-year seawater exposure may not establish a chloride ion gradient for high-quality concrete. Compared to 24 series, the Dc ratios for 50FA/50N remain relatively unaffected by the curing conditions.

This reveals that for high-strength fly ash concrete, the role of curing conditions in influencing fly ash's contribution to chloride resistance is less evident. The high-strength blast furnace slag concrete shows sound chloride resistance and low Dc with the progression of time. While the latent cementitious hydration of blast furnace slag could also be influenced by seawater temperature, apparently, the chloride resistance effect remains notably robust during the cold marine weather. The incorporation of CA2 in high-strength concrete, as observed in the 50CAW and 50CAS series, has a relatively minimal effect compared to the 50N concrete with the same curing conditions. It maybe because the ongoing hydration in seawater enhances the compactness of the high strength 50N concrete after one year of seawater exposure, while only a 7% cement replacement rate with CA2 may not yield significant effects when the concrete is sufficiently compacted. This aspect stands in distinguished contrast to the impressive performance of CA2 in the 24 series concrete. Moreover, the relatively insignificant impact on 50CA/50N compared to 24CA/24N might be linked to the adequate calcium aluminate content inherent in the cement used in the 50 series, while the CA2 additive robustly compensates for the relative inadequate calcium aluminate content in normal-strength concrete to fulfill the role of chloride binding functionality. A similar result also had been observed by Ito (2018). In high-strength SCMs concrete series, the behavior of SCM serves as an additional advantage rather than a decisive factor to drastic reduce Dc. This signifies that the water binder ratio of the cementitious matrix acts as a primary determinant for governing the penetration of chloride ions than binder types and curing methods.

2.7 Summary

This chapter manages to investigate the chloride resistance of conventional SCMs and CA2 material in steam-cured concrete under cold marine environmental conditions. Through one year of exposure to seawater, this study has provided insights into the performance of SCM concrete under three curing methods: standard curing (W), steam-air curing (S) and steam-water curing (SW). Two concrete strengths are categorized as 'normal strength' and 'high strength,' represented by the 24 series and 50 series, respectively. The observed changes in strength development, pore structure evolution, and chloride penetration in concrete are influenced by the type of SCM used and the curing method applied.

1. Before the seawater exposure experiment, 24 series revealed that the pore size distribution by MIP showed that blast furnace slag concrete had the smallest macroporosity, fly ash specimens had the largest, while CA concrete and the N concrete presented rare difference in pore structure.
2. After one year of seawater exposure, the pore structure of normal-strength steam-cured SCMs concrete continued to densify. Notably, blast furnace slag concrete consistently demonstrated low chloride diffusion coefficients (D_c) under all three curing methods, while fly ash concrete displayed a preference for post water curing and mild seawater temperature in terms of chloride resistance. 24CAS concrete exhibited an increase in porosity around a pore size of 1860nm. However, these alterations did not compromise the robust chloride resistance provided by the CA2 additive. The chloride diffusion coefficient (D_c) of 24CAS after one year of seawater exposure was only 0.53 of that of the N series.
3. The high-strength SCMs concrete series (50 series) demonstrated that the primary factor influencing chloride resistance is a low water-binder ratio. Therefore, a 7% replacement with CA2 in high-strength concrete did not exhibit a significant effect on improving chloride resistance when compared with the 50N series concrete, based on one-year data. Moreover, chloride ions did not substantially penetrate into the deeper layers of the 50 series concrete in many cases, suggesting that one year of seawater exposure may not provide sufficient time for investigation of high-strength SCMs concrete thoroughly.

CHAPTER 3

CORROSION EVALUATION OF DOUBLE LAYERS STEEL REINFORCEMENTS EMBEDDED IN HIGH-EARLY-STRENGTH STEAM-CURED SCMs CONCRETE SLAB SUBJECTED TO CHLORIDE PENETRATION

3.1 Introduction

In snowy cold regions, reinforced concrete bridges are inevitable exposed to de-icing salt environments, with increasing risks of the chloride-related corrosion (Ragab et al., 2016; Shi et al., 2012). Therefore, corrosion resistance of reinforced concrete elements is a crucial property to investigate. Supplementary cementitious materials (SCMs) show significant contributions of enhancing resistance of corrosion by compacting concrete interior and increasing ability to immobilize chloride ions (Glass and Buenfeld, 2000; Poon et al., 2000; Cheewaket et al., 2010; Kayali et al., 2012). Moreover, the improper use of reactive silica aggregate in concrete can lead to Alkali-Silica Reaction (ASR) damage, while fly ash has been employed as a measure to mitigate ASR deterioration. Hence, it is imperative to explore the ASR mitigation potential of fly ash in high-strength steam-cured concrete. On the other hand, to align the research more closely with practical engineering scenarios, high-strength steam cured specimens involving double-layered reinforcements and thick concrete layers hold relevance for applications of bridge slab in situ, which further increases the difficulty of corrosion observation. Furthermore, in the case of reinforced concrete bridge slabs exposed to de-icing salt in winter, the freeze-thaw cycles (FTC) may cause concrete cracking and surface scaling. Furthermore, the combined damage of FTC and potential ASR threats are likely to occur concurrently with chloride attack (Tanaka et al., 2017). The presence of alkali metal ions in deicing salts may activate ASR, leading to crack formation due to the expansive nature of ASR gel, potentially providing additional pathways for the transport of chloride ions (Ichikawa and Miura, 2007; Bangert et al., 2004; Heisig et al., 2016; Chatterji et al., 1987). While there have been reports suggesting that fly ash can enhance the concrete's ability to mitigate ASR development (Ichikawa, 2009; Kawabata and Yamada, 2017; Cheewaket et al., 2010), further research is needed to ascertain whether it can exert robust resistance in steam cured SCM concrete.

On the other hand, half-cell potential measurement is a commonly employed method for detecting steel corrosion in routine maintenance processes for reinforced concrete slabs. In order to maintain traffic normal functionality, conducting half-cell potential diagnosis on the upper steel reinforcement from the bottom surface of bridge slabs extends the distance between the reference electrode and the target steel measurements. The amplified thickness of the concrete cover presents obstacles in employing the half-cell potential method for diagnosing steel corrosion in bridges. Thus, there is a necessity to investigate the efficient application of the half-cell potential method to detect steel corrosion within thick concrete cover.

3.2 Research Scope

In cold regions with heavy snowfall during winter, extensive deicing salts is used to maintain traffic serviceability of bridges. Substantial amount of chloride ions from deicing salts poses a corrosion risk to embedded steel reinforcements. In continuation of the findings from Chapter 2, high-strength steam-cured concrete with fly ash and blast furnace slag effectively increased chloride resistance. Therefore, this research plans to investigate the long-term corrosion resistance of the high-strength steam-cured SCMs concrete with double-layer steel reinforcements in deicing salt environments. High-early-strength Portland cement is a common choice for high-strength precast prestressed concrete slabs in highway bridges, with more study involving fly ash and blast furnace slag as SCMs. Furthermore, investigating the applicability of the half-cell potential method for detecting steel corrosion in high-strength steam-cured SCMs concrete with thick concrete cover is also valuable.

After three-month Freeze and thaw cycles, followed by chloride penetration experiment spanning approximately three years. The chloride resistance in high-strength SCM steam-cured concrete was evaluated by comparing apparent chloride diffusion coefficients (D_c) through chloride profiles. The half-cell potential method was continuously monitoring the steel corrosion in high-strength steam-cured concrete throughout the three-year duration. Furthermore, ASR was induced in high-strength steam-cured concrete combining the damage with chloride attack. The study also evaluated whether incorporating fly ash in steam-cured concrete could mitigate ASR expansion and enhance chloride-related corrosion resistance, akin to its advantageous pozzolanic reaction observed in standard-cured concrete.

3.3 Materials and Experiments

3.3.1 Mix proportion

The reinforced concrete specimen in this study mimics a precast prestressed concrete bridge slab. The high-early-strength Portland cement followed JIS R 5210 was used. Two SCMs were adopted in this research, which are byproducts of fly ash and blast furnace slag. The double-layer steel bars with the deformed steel bars of a diameter of 19mm are arranged in a mold before concrete casting. The water-to-binder ratio (W/B) is 0.4 is applied to the control group of high-early-strength cement specimens, while the W/B for concretes incorporating SCMs is set at 0.35 to meet the high early strength requirements for precast concrete bridge. The quality of fly ash is equivalent to JIS A 6201 for the substitute ratio of cement is 20%, and blast furnace slag with an average specific surface area of 4000 m²/g conformed to JIS A 6206 replaces cement with 50%. In addition to the chloride resistance of the steam-cured concrete subjects to deicing salt exposure, the concrete spontaneously combined ASR risks are also considered. The coarse aggregate in ASR-damaged concrete specimens comprises reactive-silica andesite mixed with the original limestone at a pessimum ratio of 30%. The pessimum ratio of alkali-active andesite and limestone refers from the research of Yamada et al.

(2016). The andesite aggregate mainly consists of tridymite, volcanic glass, cristobalite, and micro-secondary quartz. Aiming to promote the initiation of ASR in high-strength specimens, in which the extra sodium hydroxide reagent was added to boost the alkali content to 5.5kg/m^3 for equilibrium relative high alkali content (RILEM AAR-3 and AAR-4). Table 10 is the mix proportion for five types of concrete. H simplified the expression of concrete that only uses high early strength Portland cement; FB refers to the specimen with fly ash added; BB is the abbreviation to the concrete incorporated with blast furnace slag. ASR specimens' marks with an A, such as HA and FBA.

Table 10 Mix proportions of high-early-strength steam-cured SCMs concrete

Series	Slump flow (mm)	Air content (%)	Unit amount (kg/m ³)							Na(OH) ₂ (kg/m ³)
			Water		Cement	Fly ash	Blast furnace slag	Sand	Gravel	
			Water	binder ratio (%)						
H	60±5	4.5±1.0	160	40	400	—	—	838	966	—
FB			154	35	352	88	—	800	959	
BB			164	35	234	—	234	781	937	
H(ASR)			160	40	400	—	—	809	925	
FB(ASR)			154	35	352	88	—	772	911	

Table 11 Experiments and specimens for high-early-strength steam-cured SCMs concrete

Specimens Type	Dimension	Experiment Intervals	Concrete types	Specimens number	Total specimens
Compressive strength	$\phi 100 \times h 200$	14	Steam-cured H, FB, BB	3	18
		28	Standard-cured H, FB, BB		
Freezing and thawing test	$100 \times 100 \times 400$	Three months	Steam-cured H, FB, BB	3	9
Accelerated length change test	$100 \times 100 \times 400$	Every five weeks	Steam-cured HA, FBA	3	6
Chloride exposure experiment	$100 \times 300 \times 128$	Depends on corrosion status	Steam-cured H, FB, BB, HA, FBA	5	25
Diffusion coefficient (Dc) followed Fick second law					

3.3.2 Specimens preparation and curing methods

Steam curing was performed in whole process for 24 hours. The temperature was set as in Figure 3.1, pre-curing for two hours, and continuously raised from the room temperature in a steam curing chamber to 65°C for four hours (rate at 1.5°C per hour), maintaining the maximum temperature for four hours, decreasing to the room temperature in the rest of duration. The maximum temperature and the heating speed are set to avoid damaging the concrete by thermal cracks and potential deformed ettringite formation (DEF). Concrete specimens cast into a designated dimensions regarding with the experiment, and the number and size are shown in Table 11.

Figure 3.2 shows the location of the reinforcements in the concrete and the specimen dimension for the salt exposure experiment. Deformed steel bar D19 specified as JIS G3112: Steel bars for concrete reinforcement, was used. Corrosion of steel bars is an

invisible electrochemical process in concrete accompanied by unpredictability because of the complex internal environment of concrete. Accordingly, five specimens were cast in each concrete type, endeavoring to yield outrageous errors. The length of the steel bars is slightly longer than that of the concrete, which aims to connect the electrodes. The exposed part of the bars is filled in epoxy resin and covered with PVC cap to prevent it from being affected by the air. At the end of steam curing, specimens without using andesite transfer to the standard curing room for six months of air curing. One month of water curing provided HA and FBA for ASR stimulating and moved to cure in the air for next five months. Subsequently, a pool of 10% NaCl solution with a size of 50 mm and 100 mm was installed in the center of the concrete upper surface to intentionally point the direction of chloride ion penetration for evaluating the activated site on the reinforcement. Waterproof alumina resin tape seals the adjacent four sides of specimens except for the top and bottom surfaces. Over the next three months, specimens underwent freeze and thaw (FTC) cycles, with the temperature changes and time intervals detailed in Figure 3.3. After the FTC, specimens are placed in a constant temperature room at temperature $40 \pm 2^\circ\text{C}$ for accelerated chloride penetration and initiation of ASR. All curing processes are presented in Figure 3.4.

Only the HA and FBA types of concrete participated in the accelerated length change experiment for ASR investigation, with experimental procedures referenced from the study conducted by Yamada et al. (2016). Three prism specimens with dimension of $100 \times 100 \times 400$ mm had been prepared for each type of concrete. Stainless steel gauge plugs were embedded beneath the concrete ends. All specimens were stored upright in sealable stainless-steel containers filled with solution. Immediately after steam curing, the initial length measurement of concrete is carried out and then stored in a constant temperature room at 60°C for two years during the accelerated length experiment. The concrete specimens were consistently wrapped in a nonwoven fabric material containing 50g of water and sealed in cling wrap into plastic boxes. Frequency of length testing is every five weeks.

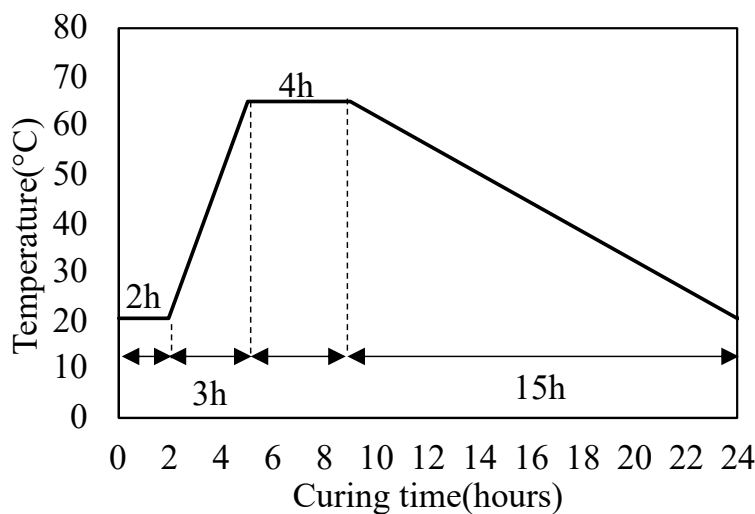


Figure 3.1 Temperature processes of steam curing for high-early-strength steam-cured SCM concrete

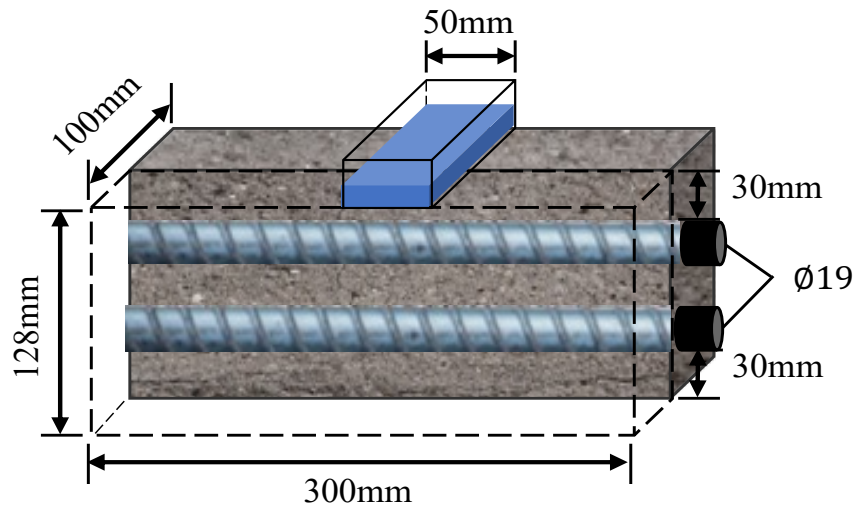


Figure 3.2 Scheme illustration of double layers reinforcements concrete with 10% NaCl solution pool (mm)

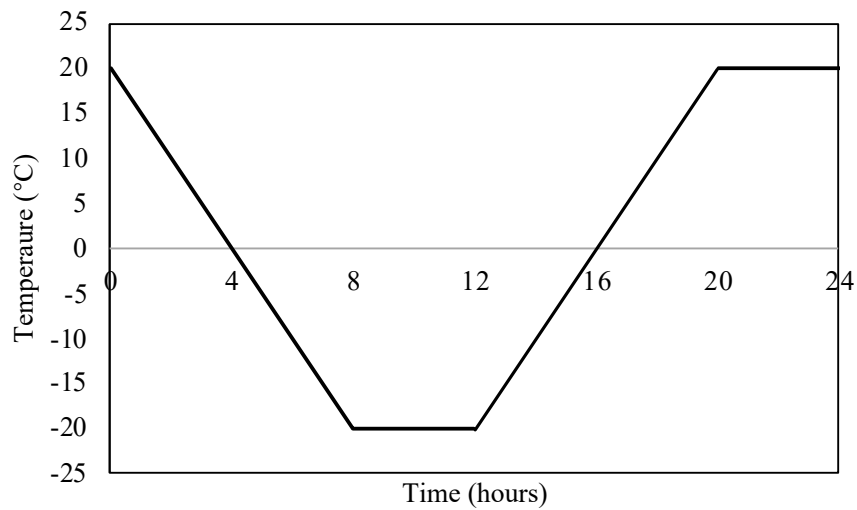


Figure 3.3 Temperature changes of Freezing and Thawing cycles in 24 hours

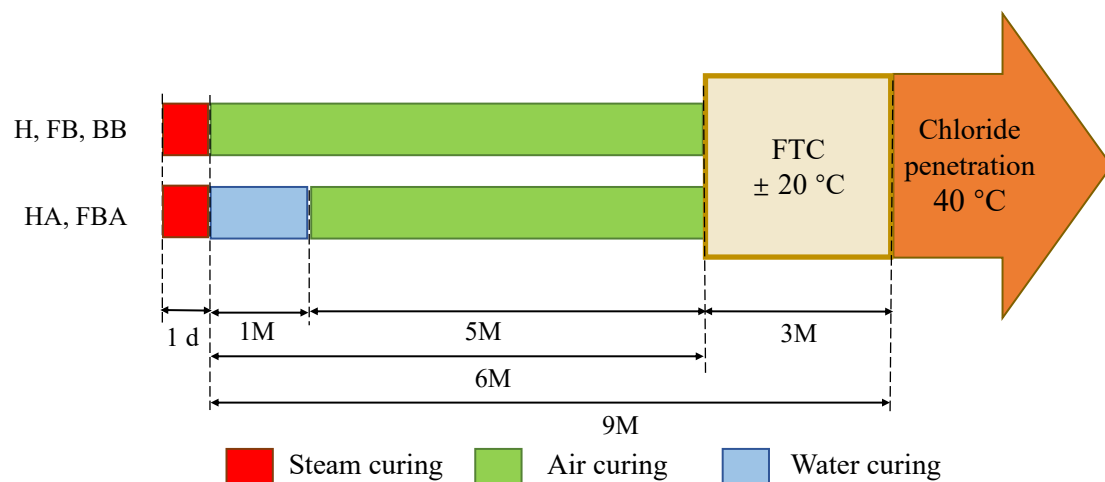


Figure 3.4 Specimen curing processes for chloride penetration experiment (d: day, M: month)

3.3.3 Electrochemical technique for corrosion diagnosis

1) Half-cell potential measurement

In this study, the half-cell potential was used as an indicator to determine the activation state of the steel bars. The experimental equipment consisted of a voltmeter and a lead/lead sulfate reference electrode. To consider real measurement on site, a total of six combinations of reference electrode (RE) placements and reinforcement connection methods is illustrated in Figure 3.5. The abbreviations used in the subsequent discussion, the upper and down layers of steel bars are U and D, and the joint two steel bars in measurement is J, which refers to the electrical connection of rebars in actual engineering. When the RE is in contact with the top or bottom concrete surface, mark as T and B, respectively. The half-cell potential of UT is the most direct response to the corrosion state of the upper reinforcement because the thickness of the concrete cover is the thinnest (Elsener et al., 2003; Andrade and Alonso, 2004; Assouli et al., 2008). However, achieving the UT combination in practical measurements on serviced bridges is challenging, so it acts a comparison group in this research. JB stands out as a promising method for assessing the condition of the upper reinforcement in concrete bridge without impacting transportation functionality. Yet, the concrete cover thickness reached 79 mm in JB measurements, potentially posing a challenge for accurate corrosion detection. On the other hand, the down bar will be monitored via DB potential.

2) Corrosion current measurements (I_{corr}) using AC impedance spectroscopy method (corrosion meter)

Furthermore, a portable AC impedance spectroscopy system has been employed for the assessment of corrosion in steel reinforcement within concrete structures by measuring the polarization resistance, which is inversely proportional to the corrosion current. Figure 3.6 illustrates the concept of the AC impedance spectroscopy (corrosion meter) provided by Yokota (1999), with the reference electrode of silver/silver chloride. In this methodology, six different combinations for RE placement on the concrete surface and the connection of steel reinforcement were also adopted, as shown in Figure 3.5. It is worth noting that a circular box with a diameter of 10 cm houses both a central counter electrode and a guard counter electrode. The corrosion meter testing method that applied in reinforced concrete, which is similar to conventional AC impedance spectroscopy. It uses both high and low frequency alternating current (AC) to polarize anode measuring polarization resistance, which also reverse the value of corrosion current. Other components in circuit, such as concrete cover resistivity, can also be determined as they function akin to capacitor charging and discharging. It should be noted that the presence of cracks on the concrete surface greatly impacts the accuracy of the corrosion meter measurements. Therefore, the test stopped at 590 days. Moreover, Andrade (2004) identified three states of metal corrosion: negligible, moderate risk, and high risk. It is recommended to increase vigilance when corrosion current reaches $0.02 \mu\text{A}/\text{cm}^2$, signaling the onset of corrosion. This study follows this level to assess the corrosion state of steel bars using corrosion meter measurements.

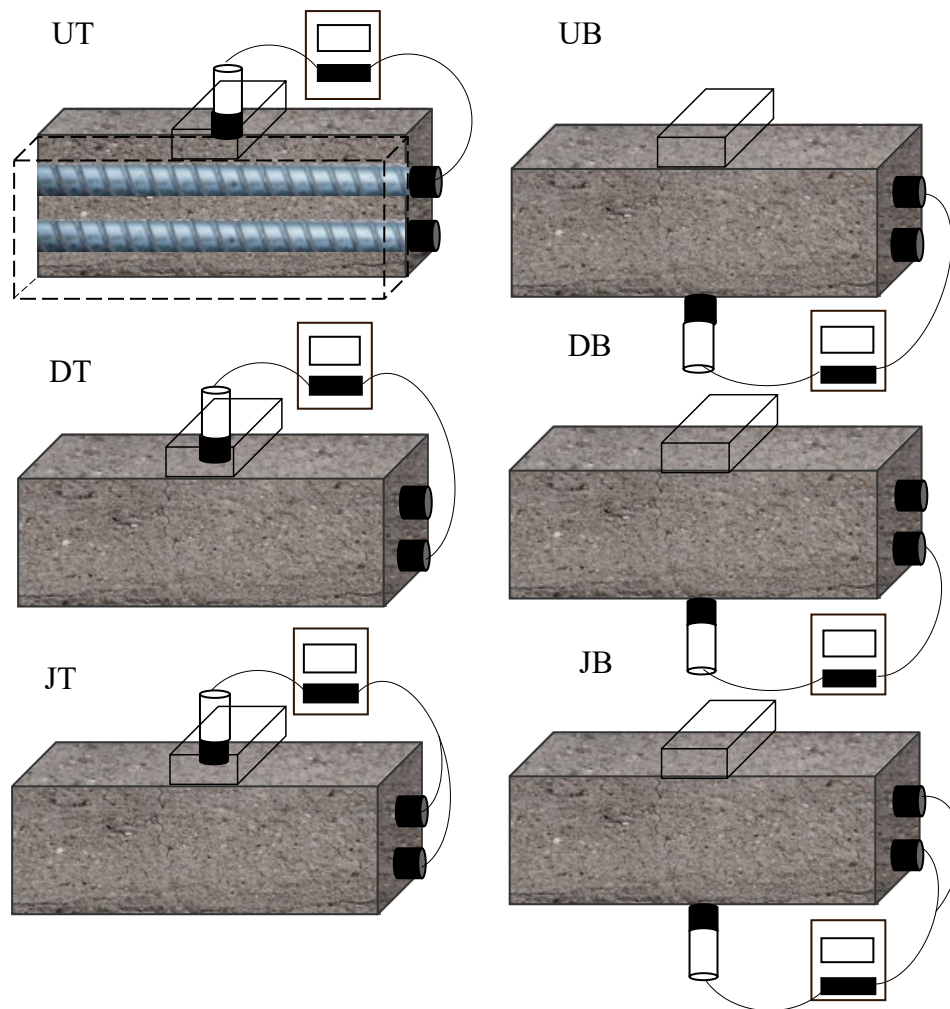


Figure 3.5 Six combinations for half-cell potential measurements

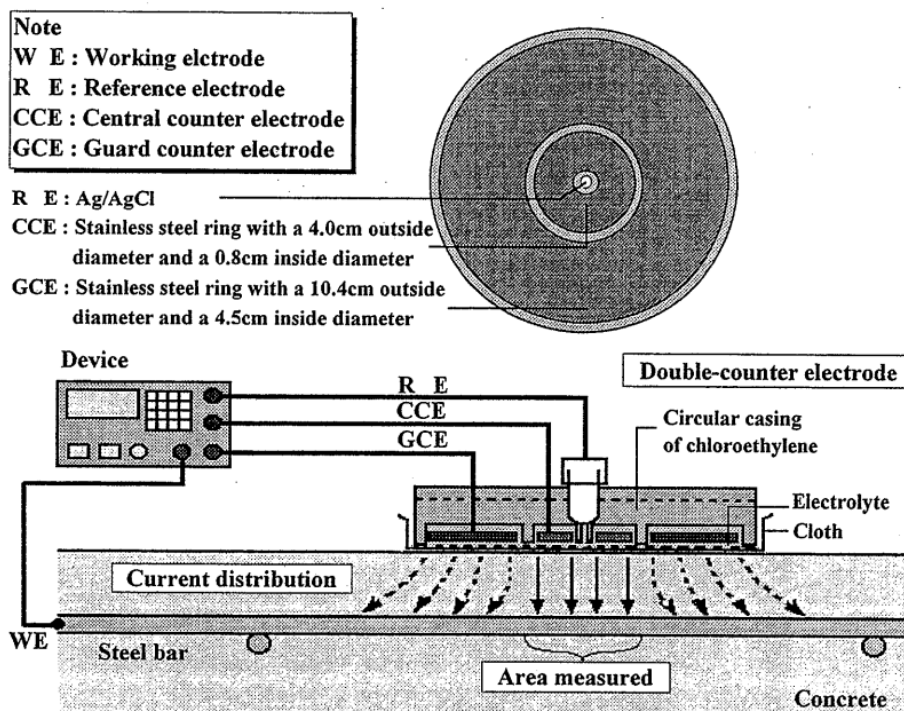


Figure 3.6 Schematic diagram of Corrosion meter (Yokota, 1999)

3.4 Properties of High-early-strength Steam-cured SCMs Concrete

3.4.1 Compressive strength

Table 12 shows the strength of steam-cured concrete for the first and 14 days and standard curing specimens for 14 and 28 days, respectively. The early strength of steam-cured specimens has reached the prestressed requirement after one day of demoulding, which saves working hours. The compressive strength of BB is lower than that of H and FB because the blast furnace slag replaces 50% of the cement mass. The strength of the steam-cured specimens at 14 days is nearly equal to that of the corresponding standard curing, which shows a slight difference from the strength development of high-strength concrete in Chapter 2.

3.4.2 Freezing and thawing test

Table 12 also provides the relative modulus of elasticity for three months and the amount of concrete spalling. It can be seen that the interior of the three concretes was not affected by the freeze-thaw cycle. However, the scaling mass loss or surface spalling of the blast furnace slag concrete was higher than that of the other two concretes because of the high-volume replacement may weak the frost resistance of concrete surface (Hou, 2017). In other words, the dense inner structure is not affected while BB exhibits weaker surface quality during the FTC test. Whether the surface quality of BB harms the results of subsequent chloride ion permeation experiments needs further confirmation.

Table 12 Properties of high-early-strength steam-cured SCM concrete

Series	Air content (%)	Scaling mass loss (g/m ²)	Relative dynamic modulus of elasticity (%)	Compressive strength (N/mm ²)			
				Steam curing (days)		Standard curing (days)	
				1	14	14	28
H	6.2	28	1.02	49.1	61.8	61.6	65.3
FB	5.8	32	1.02	48.9	60.8	60.7	66.6
BB	6.6	475	1.01	40.4	50.1	54.1	63.3

3.5 Accelerated Expansion Test of Concrete Incorporating Active Alkali Andesite

Figure 3.7 shows the length change curves of HA and FBA in the accelerated concrete prism test. According to the curves of the two types of concrete, it is clear that the concretes are suffered from expansion caused by ASR, while the initial time and the deterioration rate are diverse depending on the binders. The expansive deformation of HA was 0.133% when the first test was conducted for five weeks, and the slope of the expansion curve presented was sudden. The subsequent slope of the expansion curve gradually flattened but continued to increase until the ASR curve of HA entered a plateau around 39 weeks, and the final maximum deformation was approximately 0.27%. This represents the maximum deformation in the concrete affected by ASR, attributed to the use of the pessimum mix proportion for alkali-reactive andesite. On the other hand, the obvious length change in the FBA concrete started from the 15th week of the accelerated experiment and reached the maximum deformation 0.23% at the 86th week after a long linear growth. In the pessimum mix proportion, the function of fly ash to concrete did not eliminate the occurrence of ASR but considerably mitigated the developing rate. Also, the concrete length of concrete expansion moderated to the comparison group. It bought more time and opportunities in actual engineering to repair damaged concrete to avoid serious accidents. It demonstrates that fly ash is equally effective for high strength steam-cured concrete in inhibiting the ASR. Observations of HA and FBA in reacted andesite aggregates may provide clues to explain the efficacy of fly ash in extenuating ASR. Figure 3.8 shows photomicrographs of HA and FBA with ASR rims. Figure 3.8(a) shows two andesite aggregates undergoing different degrees of ASR and their adjacent concrete components in HA concrete. The picture on the left exhibits a remarkably obvious reaction rim at the interface between the andesite and paste, in which the aggregate has cracked due to the expansion stress accumulated in the rim (Ichikawa & Miura, 2007). No other adjacent concrete parts have been damaged yet. The picture on the right shows the ASR in a seriously degraded state, forming penetrating cracks in the andesite through to the paste and even destroying the adjacent limestone. Calcium alkali silica might flow into the limestone along the crack track and dry up to a white solid. The andesite on the left side of Figure 3.8(b) has started to react and has formed a clear ASR rim around the grain. In the current stage, the expansive stress inside the rim has not yet caused damage to the andesite and surrounding component. The andesite on the right of picture (b) has deteriorated to a severe degree, and the ASR gel has migrated into the crushed aggregate. But it does not cause the thorough crack as in HA and further affects other concrete components. It may attribute to the fact that the pozzolan of fly ash competes with ASR for alkali, reducing the worst damage state, which corresponds to a lower maximum deformation of FBA than that of HA. It may not produce blind negatives for the formation of ASR gel and corresponding expansion stress. To a certain extent, the flowing ASR gel may cover the steel bar to prevent oxidation reaction during oxygen contact, or the resulting expansion can compress the concrete interfacial zone (ITZ).

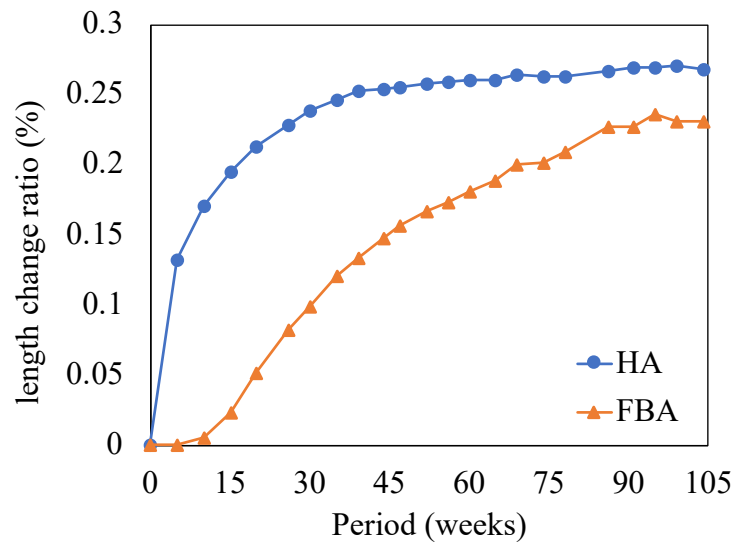


Figure 3.7 Results of accelerated length change experiment

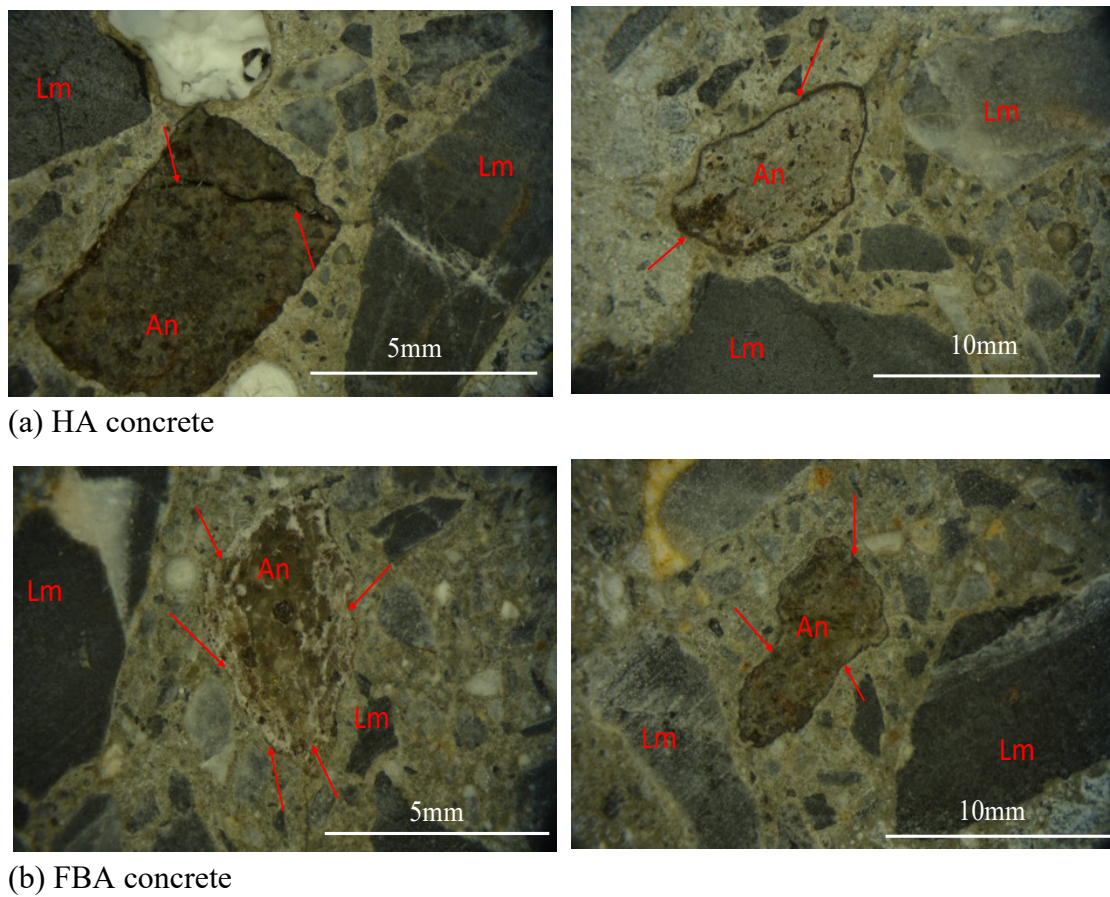


Figure 3.8 Active andesite and surrounding composition of concrete: (a) HA concrete and (b) FBA concrete

3.6 Corrosion Evaluation via Electrochemical Technique

3.6.1 Corrosion diagnosis of double layer rebars using half-cell potential method

1) Diagnosis of onset of corrosion via half-cell potential method

Figure 3.9 gives all the half-cell potential curves with six combinations of the five concrete mixes. Next, the steel state analysis is carried out on the curve trends changes. The trend of the curves roughly divides into two types, one of which is that the state of the horizontal line is always maintained, and the potential value is approximately above -200mV.CSV . The other is that the curve shows a downward trend. Since the corrosion monitoring conducts on all specimens from the first day of the salt exposure experiment, the possibility of steel corrosion is extremely low. Hence, it can be judged that the reinforcement is passive when the potential curve shows little decrease. Some specimens of FB and BB show an increase of potential value with experiment time because the concrete continued to hydrate being dense. The sudden change in the potential value most likely indicates the initiation of steel bar activation due to generated corrosion current, especially the drop of potential exceeds by 100mV , as observed in this study. A slow decline phenomenon of potential curves, mainly in which the concrete contains fly ash. Additionally, the potential curve of FBA2 and FB4 temporarily drops and then rises back. These situation needs to consider the complexity of pozzolanic reaction. Furthermore, there are the reduced oxygen content in the ITZ between steel and concrete and the increased concrete conductivity because of the penetration of the external salt solution. Another intriguing phenomenon observed in the corrosion of the upper rebar stems from the potential difference between DB and JB. When the upper rebar in concrete is in a passivated state, the curves for DB and JB almost entirely overlap, where the potential difference between them does not exceed 30mV . However, once the UT potential experiences a drop exceeding 100mV , the curves for DB and JB significantly diverge, resulting in a potential difference of over 100mV . Furthermore, in cases of the specimens without the presence of ASR-threatened where corrosion potential is detected in the lower rebar based on DB potential values, the potential difference of DB-JB returns to within 100mV . A similar trend is also observed in HA and FBA, although the potential difference between the two connection methods does not narrow to within 100mV as markedly. It is necessary to emphasize that some definitions are related to different phenomena of the trend of the half-cell potential curves, so two draft definitions are given below:

Definition one (D1): Between two adjacent potential measurements, JB potential drop more than 100mV.CSV and no rise above the potential of -200mV.CSV in the subsequent experiments, the latter date determines as Corrosion Initiation (T_i) for upper bar, while the JB potential change in FBA concrete is 70mV.CSV .

Definition two (D2): An absolute potential difference exceeding 100mV between DB and JB indicates the potential onset of corrosion in upper rebar, while a return of the potential difference to within 100mV suggests possible corrosion of the lower rebar.

For the cases, the potential curve drops gradually (drop difference lower than -50mV) until the potential value drops below -350mV as the beginning of corrosion, which is regarded from ASTM C 876.

The estimated Ti of upper rebar and down bar by referring UT, JB, DB-JB, and DB potential, are listed in Table 13, as per the definitions of D1 and D2, for all concrete specimens. Ti is devoted to the average days of the onset of depassivation. According to the Ti reference value of UT, the upper steel bar of HA corrodes foremost on 179 days, followed by FBA on 328 days and H on 455 days. In BB, only the potential value of BB5 drops suddenly on 504 days. FB specimens show no corrosion during the duration of corrosion monitoring. The upper reinforcement Ti of HA, the concrete containing the andesite with the pessimum ratio, was 276 days earlier than that of the comparison group H due to the influence of ASR. The Ti of FBA is 149 days later than HA, and it is more than 100 days earlier than H concrete. The DB potentials expressed by the Ti of the underlying reinforcement of each concrete were HA: 657 days, H: 671 days, and FBA: 749 days, while no corrosion traces were detected for FB and BB concretes. The distinct in the Ti between the upper and lower bar is that HA seems unaffected by ASR and occurs equally in onset time as H. FBA prolongs the Ti time and two specimens that do not show a drop in DB potential during the whole experiment. It appears that ASR affects the upper and lower bars differently, accelerating the activation of the upper layer but relatively prolonging the corrosion initiation of the down bars.

Table 13 Estimated corrosion initiation (Ti) via the half-cell potential method

	UT (days)	JB (days)	DB-JB (days)	DB (days)	Ti (days)			
					UT	JB	DB-JB	DB
H1	420	420	420	679				
H2	420	420	420/714	679				
H3	336	336	336/588	504	455	452 (4)	462	671
H4	679	630	672	700				
H5	420	-	462	795				
HA1	154	154	154	875				
HA2	168	168	168	679				
HA3	210	224	210	420	179	185	189	657
HA4	140	140	140	630				
HA5	224	238	259	679				
FBA1	336	336	420	679				
FBA2	420	-	420	-				
FBA3	378	462	420	679	328	378 (4)	365	749 (4)
FBA4	210	420	273	679				
FBA5	294	294	294	960				
BB5	504	504	504	-	-	-	-	-

2) Corrosion current measured by Corrosion meter (AC impedance spectroscopy)

The corrosion current of the specimens was measured using a corrosion meter at intervals of 224, 316, 407, 496, and 590 days. H, HA, and FBA specimens were tested on most experimental dates, while FB was tested only on days 316 and 590, and BB was tested only on day 590. The specific measurement durations for each specimen are listed in Table 14. Due to the relatively complex operational procedures of the corrosion meter compared to the half-cell potential method, corrosion current testing is conducted when there are suspicious changes in the half-cell potential. Table 15 lists the corresponding days when corrosion currents exceeding $0.02 \mu\text{A}/\text{cm}^2$ were detected for upper steel reinforcements by UT, along with concrete layer resistances. The resistance is used to characterize the properties of the tested concrete layer, without emphasizing the calculation of concrete resistivity. Additionally, data for JB is included for corrosion in the upper steel reinforcement. In the case of the FBA2, the corrosion date is an exception as it does not coincide with the initial occurrence of corrosion current exceeding $0.02 \mu\text{A}/\text{cm}^2$, which is about $0.023 \mu\text{A}/\text{cm}^2$ at 224 days. This anomaly arises due to subsequent tests revealing an almost non-change in I_{corr} of $0.024 \mu\text{A}/\text{cm}^2$ at 316 days and the I_{corr} lower than $0.02 \mu\text{A}/\text{cm}^2$ at 407 days. This process may suggest that the corrosion initiation stage for FBA2 has a significantly extended duration, whereas for other specimens, the transition from the initiation stage to the corrosion propagation stage is relatively short, possibly owing to the influence of fly ash. However, the corrosion propagation stage is not the primary focus of this study, and there may be opportunities for further discussion in future research. The 496-day interval presented here based on the I_{corr} increased to $0.035 \mu\text{A}/\text{cm}^2$. At the same time, the resistivity of FBA2 decreased significantly from the previous test. This underscores the importance of employing analytical judgment alongside pure numerical values. The corrosion current of Table 15 closely corresponds to the date of estimated corrosion onset by the half-cell potential (Table 13). It significantly enhances the reliability of estimating the corrosion initiation date for the half-cell potential method.

On the other hand, the corrosion meter's JB I_{corr} struggles to provide valuable signals regarding corrosion initiation. Furthermore, the I_{corr} for the JB combination should theoretically behave of UT when corrosion just begins. However, Table 15 only shows a 1/3 match, even with a discrepancy as high as 66 times. This complicates the estimation of steel corrosion initiation and propagation using JB, due to the complexity of concrete internal environment and the interface of steel-concrete.

Subsequently, we refer to the concrete layer corresponding to UT combination as the "UT layer" and that for JB as the "JB layer." Observing the resistivity value of the UT and JB layer during corrosion initiation reveals its dependence on binder type and curing time. The resistivity values of the UT layer for HA and H remain largely unaffected by time, staying below $0.4 \text{k}\Omega$, while the JB layer exhibits significantly different trend. This difference is not only because H has a longer time before corroded allowing for more hydration, but also it shows that the impact of the ASR damage on HA concrete is overall. In the case of FBA specimens, the upper limit of Res in the UT

layer can approach 3 k Ω , while the JB layer can reach from 4.2 k Ω to 9.7 k Ω . This result confirms that the effective inhibitory effect of fly ash on ASR in high-strength steam-cured concrete. The JB layer's resistivity reaching 7 to 9 k Ω is almost an order of magnitude different from HA's, indicating that fly ash concrete can still act as dense concrete, even in the presence of ASR-related hazards. The resistivity values at the onset of corrosion in HA and FBA differ by nearly an order of magnitude, which is the precise reason why corrosion initiation in the upper layer rebars of FBA is delayed by about 150 days compared to HA.

To calculate the concrete resistivity for the UT and JB portions when corrosion occurred in each concrete, an outlier detection method with a threshold of 1.5 times the standard deviation was applied. According to the above rules, the UT resistivity of H3, as well as the JB resistivity of HA3, H3, and FBA2, can be filtered out, and the results are displayed in Table 15. The resistivity of upper part concrete between H and HA is mere difference when corrosion begins in the upper bars. It suggests that ASR cracks seem have no additional impact for the resistivity of the UT part, where the concrete exposed to salt pool directly. Conversely, a significant difference in the lower concrete, which is not only because JB part of H concrete has a dry condition and a longer curing duration, but also ASR damage decrease the JB resistivity of HA due to ASR gel. It also indicates that ASR cracks extend throughout the entire concrete specimen, although the state of damage development may vary within the concrete. In the case of FBA specimens, the average of corroded resistivity in the upper layer of concrete is around 2.51 k Ω , while the JB layer shows 8.63 k Ω . However, the effectiveness of fly ash in densifying FBA concrete is indeed reduced compared to the electrical resistivity of FB at 316 days, with a decrease of approximately 0.3, as shown in Appendix F. This reduction is attributed to the presence of ASR risk in FBA.

3.6.2 Six combinations of half-cell potential measurements

Figure 3.9 reveals an interesting observation: the half-cell potential curves of reinforcement placed on the same side of the concrete typically exhibit overlapping patterns before any suspicious corrosion-related potential drop occurs. This could be attributed to the fact that, in the absence of significant corrosion activity causing notable changes in potential, the potential values exhibited by various connection methods primarily depend on the closest electrode to the reinforcement. As the UT curve displays a downward trend, similar decreases in UB, JT, and JB potentials are also evident. In contrast, DT and DB, which are linked to the corrosion activation state of the lower reinforcement, maintain relatively high potential values. The reduction in potential curves for DT and DB suggests possible depassivation of the lower bars.

Conversely, when the upper bar may occur corrosion, various combinations connected to the upper rebar exhibit a shared point of simultaneous decline, although the magnitude of the potential drop varies. Notably, the JB combination stands out in this study, its curve changes synchronously with UT, regardless of the reinforcement's corrosion state. Although the potential value at the time of the sudden drop may fall

below 100mV, this could be due to reduced sensitivity caused by the concrete layer thickness. Referring to the change in JB values closely mirroring the UT potential drop, it is defined that JB's potential suddenly drops to more than 70mV. According to the new FBA standard, JB's Time to Initiation (T_i) is concluded to be 378 days.

On the other hand, the similarity in the corrosion response of the DB-JB potential with the UT potential can be explained. When both upper and lower rebar in concrete is in a passivated state, with very weak potentials, the electrically connected JB potential is primarily influenced by the lower rebar, resulting in close proximity between the half-cell potentials of JB and DB. However, once anodic reactions on the upper rebar start to generate significant potentials, which leads to a notable separation between the potential curves of JB and DB because DB-JB lies in its ability to mitigate interference from the concrete layer to some extent, as both DB and JB are embedded in a thick concrete layer. Therefore, almost all corrosion detected by UT is also rapidly reflected by DB-JB, while JB may be disrupted by the concrete layer and unable to indicate corrosion. However, the advantage of DB-JB in mitigating the influence of the concrete layer is not as pronounced when assessing the corrosion of lower rebar in concrete affected by ASR. This is because ASR-affected concrete is damaged in proximity to the harmful source, while the concrete layer in a state with no significant ASR reaction exhibit sound. Furthermore, the drawback of DB-JB is for increased labor. Using the DB-JB method in bridge maintenance means testing the potentials at all points by two connection methods, even if the lower rebar is reliable with corrosion-free. This contradicts the desire for a quick and convenient assessment of rebar corrosion status. Nevertheless, DB-JB can still be used for corrosion detection in upper rebar when JB potential alone cannot provide a conclusive assessment.

3.6.3 Efficient corrosion diagnosis through JB potential measurement

The relationship between JB and UT is discussed in Figure 3.10. The scatter distribution of JB-UT shows roughly two zones in different types of concrete. The first zone represents the overlapping scatter points of JB-UT potential within a specific potential range, where higher potential values of scattered points are considered to be low reactivity of the upper reinforcement. Figure 3.10(f) displays the respective JB and UT thresholds for the five concrete types, except for the JB potential threshold of FBA. In theory, ASR-induced microcracks accelerate solution penetration into the concrete interior, reducing concrete resistance. Additionally, the pozzolanic reaction in FBA, occurring simultaneously with ASR damage and chloride attacks, affects the measured values of the half-cell potential. Otherwise, these discrepancies could stem from potential errors in detecting steel corrosion, especially within the complex interior environment of the concrete cover. This significance is evident in the preparation of five specimens for each concrete type.

When the potential values of UT and JB exceed the threshold value above, the JB-UT curve decreases linearly, which implies that the steel bar has been depassivated and started corrosion propagation. Table 13 also provides the JB corrosion onset time in

each concrete specimen, which is highly compatible with the UT time in H and HA, while the diagnosis on three upper steel bars in FBA shows no corrosion. The T_i of H and HA obtained by JB potential are 452 days and 185 days, respectively. Conversely, the T_i of H5 is difficult to determine by JB potential monitoring because the potential difference between adjacent measurement is lower than 50mV. If referring to ASTM C876, the JB potential decrease below -350mV occurs 210 days later than the UT display. Furthermore, there is a delayed response observed in the T_i indicated by JB compared to the UT potential in D2 for FBA. When JB suddenly dropped, it was later than UT about 210 days, which may attribute to the pozzolanic reaction of fly ash considerably enhanced the resistivity of the lower concrete layer in FBA, thus it cannot provide the transportation channel of humidity as much as the upper part of concrete.

Based on the potential threshold illustrated in Figure 3.10(f), the localized concrete densification due to the pozzolanic reaction might influence the accuracy of JB potential detection. This could be explained by ASR-induced cracks in FBA, allowing salt solution to penetrate the cracks, reducing concrete resistivity, and impacting diagnostic results. Upon adjusting the JB corrosion definition based on concrete types, the T_i of JB potential for FBA is determined to be 378 days. This highlights the sensitivity of the JB potential method to concrete binders and suggests separate considerations. Overall, in high-strength steam-cured concrete, the JB combination effectively communicates corrosion information for upper steel bars. Despite JB potential unable to provide a threshold for FBA, the JB potential monitoring method still assesses the corrosion status of upper steel bars effectively.

3.6.4 Corrosion resistance of high-early-strength steam-cured SCMs concrete

The corrosion resistance of the five concrete mixes in this study was evaluated by comparing the estimated T_i for each mix using half-cell potential monitoring (Table 13). The manifestation of corrosion was initially observed in the upper bars of the HA mix, followed by FBA and H. The T_i for the upper bars in FBA is 1.8 times that of HA but 127 days earlier than H, indicating that fly ash has the ability to control ASR development but not eliminate it entirely. Additionally, varying degrees of ASR in both the upper and lower concrete sections of FBA provide an advantage in delaying the corrosion of the lower reinforcement. The five steel reinforcement bars in the FB concrete exhibited stable half-cell potential behavior throughout the observation period. However, BB5 was the exception, as it displayed a sudden drop in potential. This drop could be attributed to surface damage caused by freeze-thaw cycles or salt scaling, which likely facilitated the ingress of salt solution. Subsequent observation experiments validated the passivation of steel bars in the FB and BB specimens, with the exception of BB5. It suggests that steam-cured high-strength fly ash and blast furnace slag concrete improved corrosion resistance comparable to that of normal concrete.

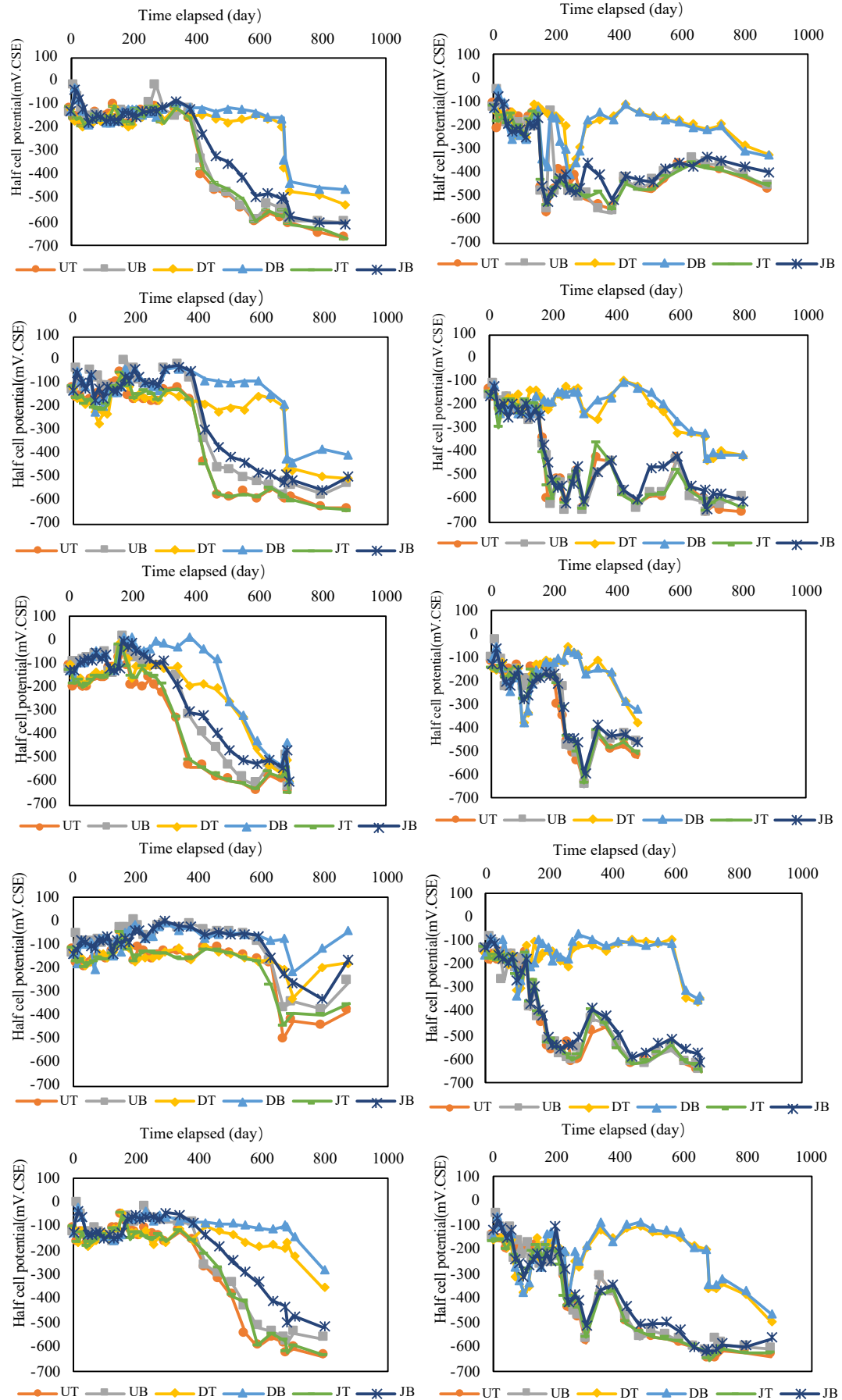
Table 14 Durations for Corrosion meter measurement in each series

	Duration of Corrosion meter measurement (days)				
	224	316	407	496	590
HA	●	●	▲	▲	×
H	●	-	●	●	●
FBA	●	●	●	▲	▲
FB	-	●	-	-	●
BB	-	-	-	-	●

“●” represents valid data for five specimens in the same type of concrete on the experiment date; “▲” indicates data from one or some specimens in the same type of concrete are less reliable due to cracks, these data are dismissed; “×

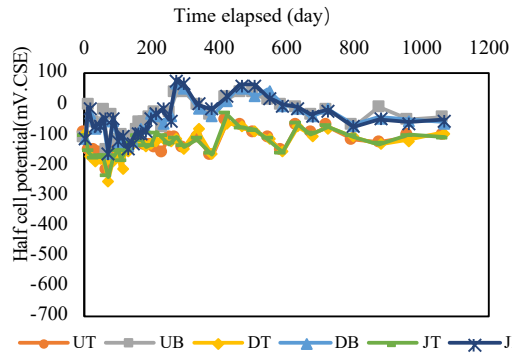
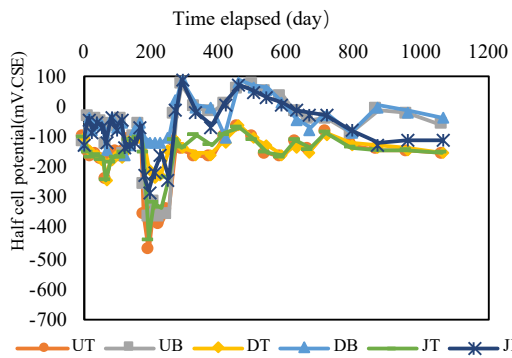
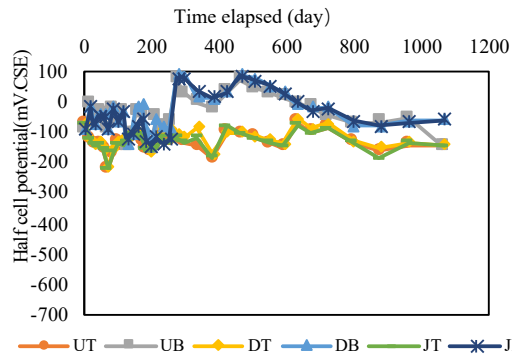
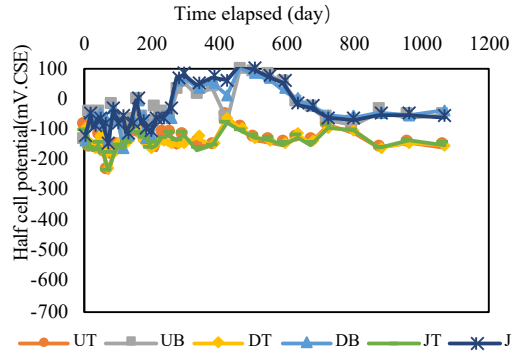
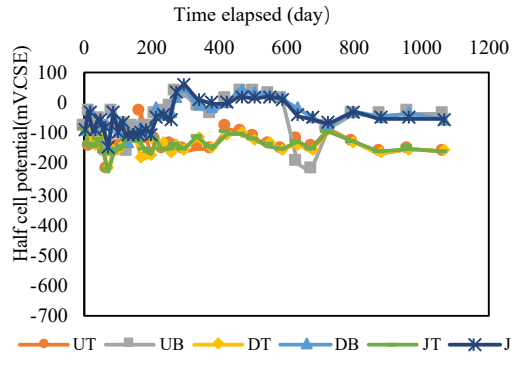
Table 15 Corrosion current (Icorr) and concrete cover resistivity (Res) measurements via Corrosion meter

	No.	Interval (days)	Icorr ($\mu\text{A}/\text{cm}^2$)		Icorr ratio	Resistivity ($\text{k}\Omega$)		Average Resistivity ($\text{k}\Omega$)		Average Res ratio
			UT	JB		UT/JB	UT	JB	UT	
HA	1	224	1.186	0.133	8.9	0.27	0.69	0.29	0.67 (4)	0.43
	2	224	1.932	0.834	2.3	0.27	0.53			
	3	224	0.211	0.101	2.1	0.31	0.96			
	4	224	0.612	0.155	4	0.24	0.76			
	5	224	0.155	0.073	2.1	0.34	0.68			
H	1	496	0.829	0.012	66.9	0.41	12.91	0.31 (3)	12.8 (3)	0.024
	2	496	1.985	0.14	14.2	0.26	12.68			
	3	224	0.021	0.014	1.5	1.13	7.83			
	4	-	-	-	-	-	-			
	5	496	1.985	0.14	14.2	0.26	12.68			
FBA	1	316	0.032	0.014	2.2	2.32	7.13	2.51	8.63 (4)	0.29
	2	496	0.035	0.012	3	2.46	4.19			
	3	496	0.039	0.006	6.6	2.84	8.81			
	4	224	0.072	0.001	66.2	2.93	8.94			
	5	316	0.093	0.015	6.3	1.98	9.65			
BB	5	590	0.275	0.014	19.9	7.38	8.83	-		

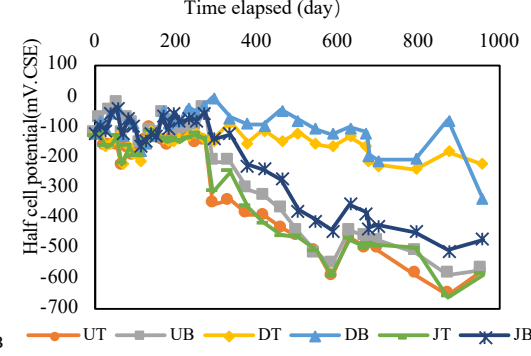
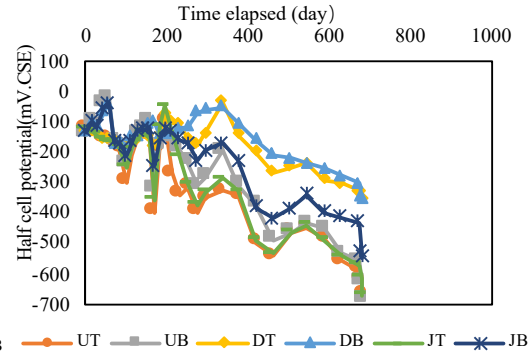
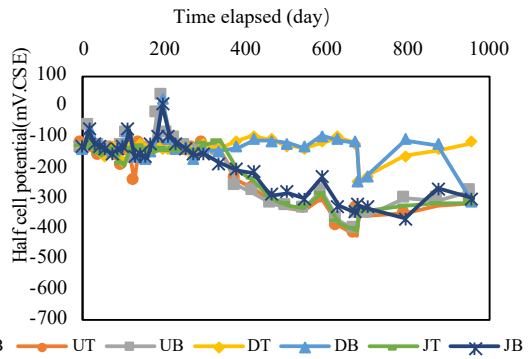
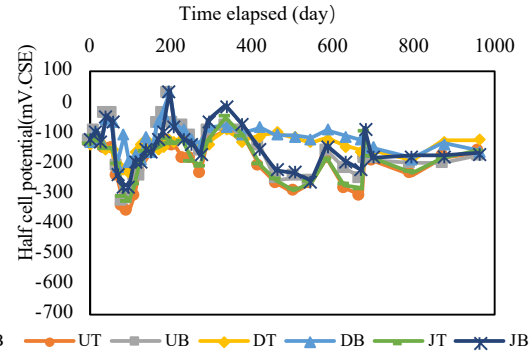
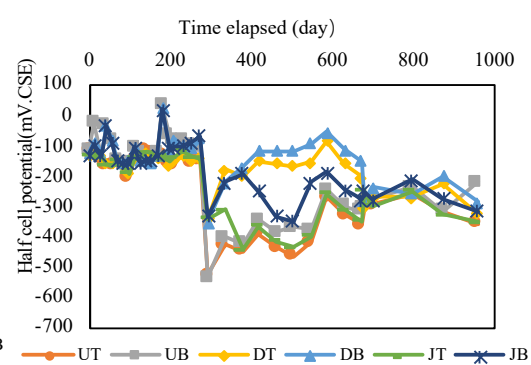


(a) H concrete

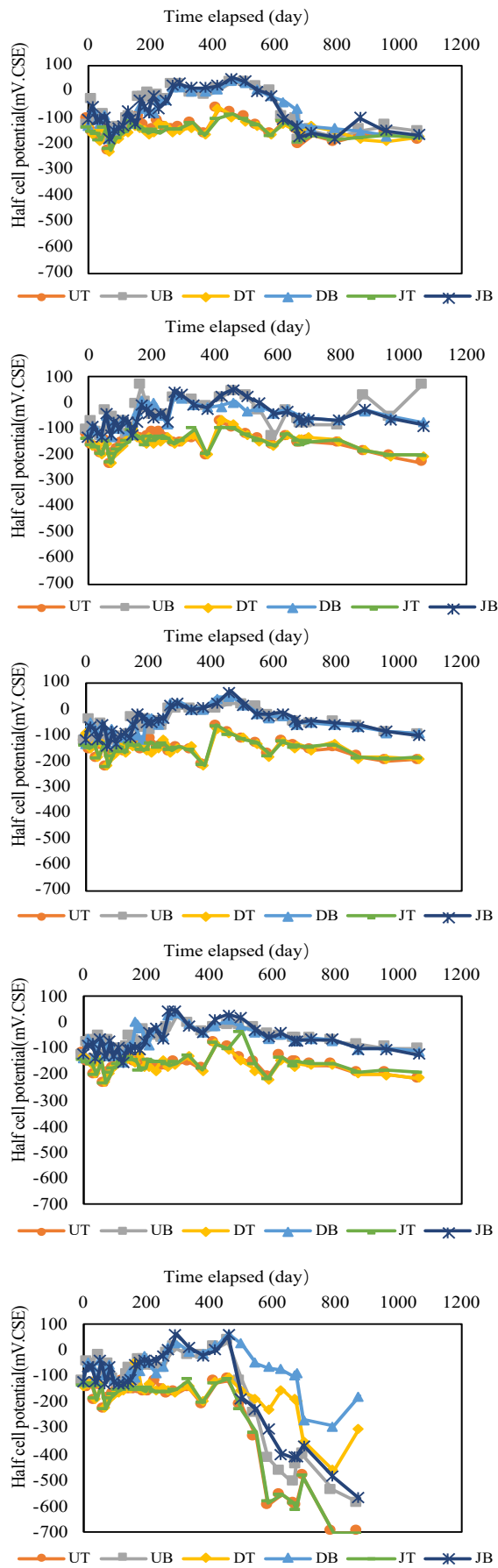
(b) HA concrete



(c) FB concrete

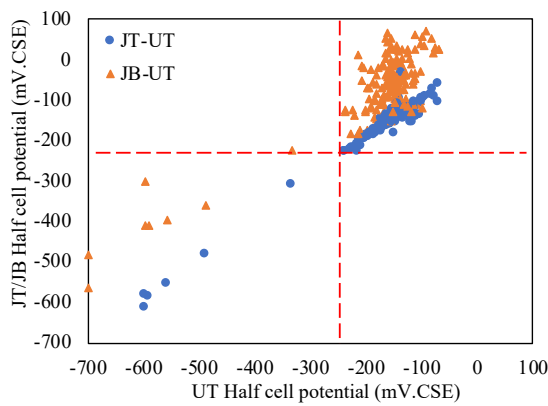
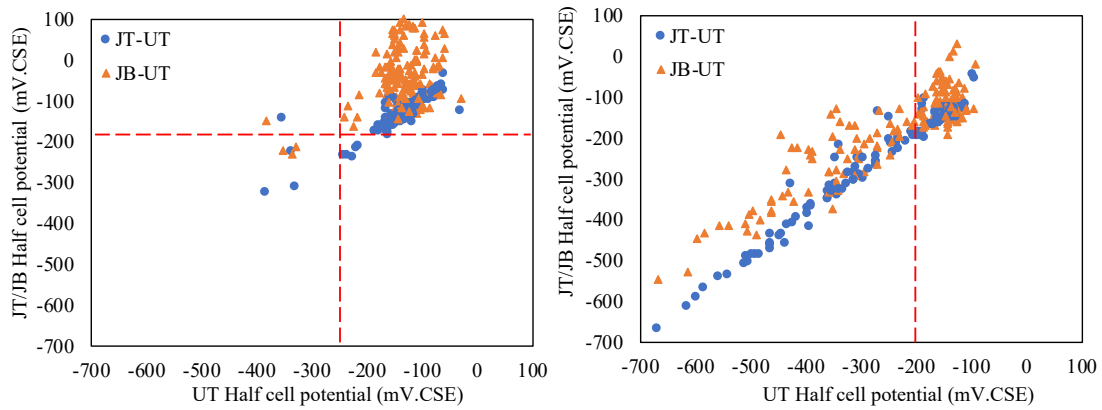
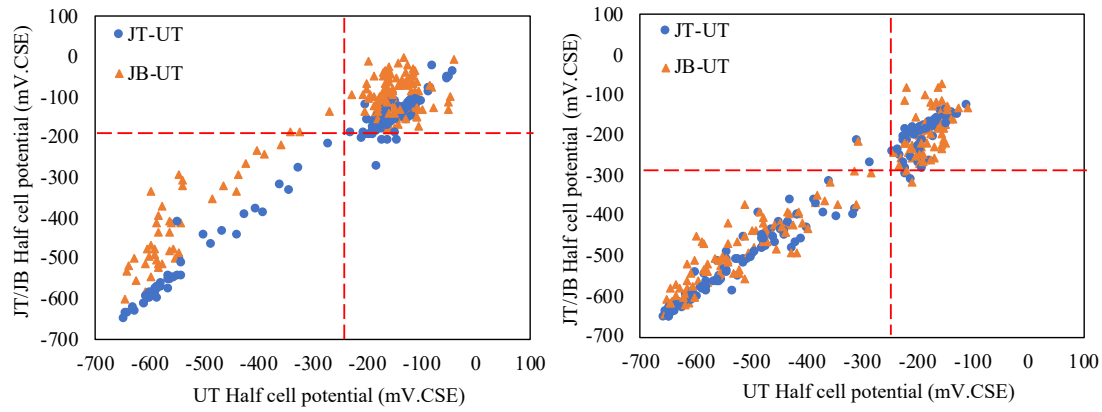


(d) FBA concrete



(e) BB concrete

Figure 3.9 Half-cell potential of five types of concrete



	H	FB	BB	HA	FBA
UT (mV. CSV)	-250	-250	-250	-250	-200
JB (mV. CSV)	-200	-200	-200	-300	-

(f) UT and JB potential threshold for upper rebar in five types of concrete

Figure 3.10 Scatter plot distribution of JB-UT and JT-UT for five concrete types: (a) H (b) HA (c) FB (d) FBA and (e) BB concrete with (f) UT and JB potential threshold before upper rebars corrosion initiation (Ti)

3.7 Appearance of Concretes and Steel Bars after Long-term Chloride Exposure Experiment

3.7.1 Specimens of H, FB, and BB concrete

Figure 3.11 shows the morphology of the H, HA, FB, FBA, and BB concretes at different test dates and the corresponding actual reinforcement states. Table 16 gives the exact dates of concrete split and the associated state of the reinforcement, where the corroded reinforcement is abbreviated as "C", and "P" means remain passive. Some concrete surface exhibits cracks along the direction of the reinforcement, which refers to as longitudinal cracks in the following. These cracks are formed by the extrusion damage caused by the corrosion products of steel bars. When corrosion cracks appear on the surface of the concrete implies that the destroyed level is more severe near the reinforcement. The formation process of cracks on the concrete surface has been observed in this experiment. Generally, a thin crack starts to form in the salt pool area, barely visible at the initiation. Rust can also release through this crack to the concrete surface (brown traces of H2, H3, HA4 and FBA4). Next, the micro-cracks gradually widen and spread out of the salt pool area (H5 is a salt solution leakage). Then the initial crack is gradually widened at the center, and the crack is elongated in the longitudinal direction until the upper surface is separated.

The surface of the H concrete shown in the picture is the day when the corresponding steel bars were taken out. H1, H2 and H3 have through longitudinal cracks with a width of wider than 5 mm. Extensive corrosion damage occurred in the upper reinforcement of the three specimens, which could explain the wide cracks in the respective concrete surfaces. However, H3 only has a small area of corrosion at both ends of the lower steel bar, while H2 remains intact. In this case, the upper steel bar has a large area of corrosion, but the lower steel bar only has a small, corroded area at the ends. It may be explained that salt solution flows vertically to the deteriorated steel bar and spreads to other places along the expansion cracks. H5 has thin cracks that spread from the salt pool part to the outside, while the surface of H4 has no harm. However, the embedded upper rebars in H4 concrete shows a pit corrosion but holds a sound surface, while the down bar remains passive. It appears that the corrosion status of the lower steel bars in H4 may have been misjudged based on the UT and JB half-cell potentials. Specifically, the rebound in the half-cell curve of H4 after a significant drop may imply that the steel bars remain in good condition. This underscores the importance of monitoring the corrosion status of steel bars. Accordingly, the longitudinal cracks on the surface of H concrete may be related to the occurrence time of corrosion on the upper reinforcement. Moreover, the salt solution penetrates in the direction of gravity, so it is usually considered that the upper surface of the steel bar that comes into contact first is vulnerable to gathering more corrosion products. The cross-shaped cracks of H2, H3 and BB5 indicate the part subjected to the relative larger expansion stress due to the corrosion. In fact, the corrosion site of steel bars and surrounding space are full of uncertainty. Corrosion of reinforcement can be severe even when invisible deterioration of the concrete surface. Based on the corrosion position of the down steel bars the cracks

caused by the corroded upper bars led down bar being partially in contact with the salt solution and air. In other words, the concrete cracks caused by the corroded upper bar may affect the condition for the down steel bar, so timely diagnosis and repair of steel corrosion in field engineering are crucial. The steam-cured concrete incorporates fly ash and blast furnace slag to maintain an outstanding concrete surface condition, except for BB5, where the upper and down steel bars are damaged.

Table 16 Verified corrosion condition of rebars in observation experiment

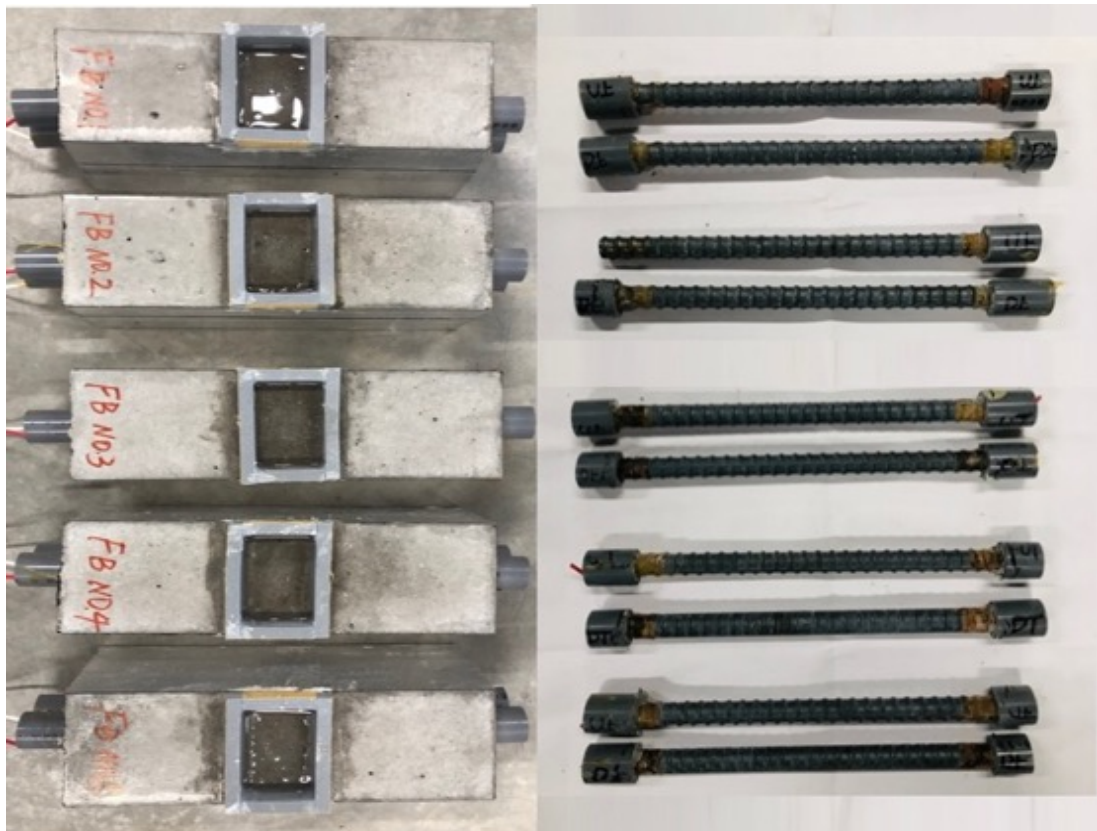
Series	Double layer rebars	Specimen number				
		1	2	3	4	5
H	Split(days)	1102	1102	694	1064	1054
	Upper	C	C	C	C	C
	Lower	C	C	C	P	C
HA	Split(days)	1064	1102	490	679	1102
	Upper	C	C	C	C	C
	Lower	C	P	C	C	C
FB	Split(days)	1210	1210	1210	1210	1065
	Upper	P	P	P	P	P
	Lower	P	P	P	P	P
FBA	Split(days)	1035	1035	1035	694	1035
	Upper	C	C	C	C	C
	Lower	P	P	P	C	C
BB	Split(days)	1065	1210	1210	1210	678
	Upper	P	P	P	P	C
	Lower	P	P	P	P	C



(a) Appearances of H concrete (H1, H2, and H4 on 1051 days; H3 on 692 days; H5 on 799 days), rebars on the split date



(b) Appearances of HA concrete (HA1, HA2, and HA5 on 1083 days; HA3 on 490 days and HA4 on 663 days), rebars on the split date



(c) Appearances of FB at 1064 days, rebars on the split date



(d) Appearances of FBA concrete (FBA1, FBA2, and FBA3 1031 days; FBA4 and FBA5 on 692 days), rebars on the split date



(e) Appearances of BB concrete at 1065 days (BB5: 678 days), rebars on the split date

Figure 3.11 Appearances of five types of concrete (a)H, (b)HA, (c)FB, (d)FBA, and (e)BB concrete before/on the split date, rebars on the split date (Table 16)

3.7.2 Specimens of HA and FBA concrete

Both HA and FBA concrete surfaces have different degrees of chapped cracks that are considered ASR-related cracks. Figure 3.12 shows the specimen of HA3 on 490 days. The red lines on the specimens are marked as ASR cracks. The concrete top surface of HA1, HA2, HA3, and HA4 also shows wide longitudinal cracks, but the extent was far less wide and elongated than that of H concrete, even though the upper bar of HA suffered extensive corrosion. The sudden drop in the potential of the upper rebar in HA5 is the last one, while the longitudinal cracks of HA5 only extend to one end. In the case of HA, the emergence of longitudinal cracks appears to be linked to the corrosion of the upper reinforcement. However, the less noticeable ASR cracks in the HA specimens developed prematurely compared to the longitudinal corrosion cracks. This phenomenon also aligns with the rapid expansion of HA observed in length change experiments, though ASR cracks on the top surface of concrete undoubtedly enhance the penetration of chloride ions into the concrete. On the other hand, the corrosion cracks on the surface of HA are relatively less extensive compared to those on H. Furthermore, the cracks resulting from the expansion of active andesite particles could potentially create storage space for corrosion products and subsequently reduce the extent of longitudinal cracks on the concrete surface. The lower bar of HA is barely affected by the longitudinal corrosion cracks caused by the upper steel bar. In fact, the Time to Initiation (Ti) of the lower rebar of HA is postponed to nearly as late as that of H, while the lower bar of HA2 even shows no signs of corrosion until the end of the experiment. There are several considerations to discuss regarding the delayed corrosion observed in the underlying steel bars of HA. It is important to note that within the same concrete specimen, the degree of ASR development may vary, with ASR damage being more pronounced closer to salt solutions. Consequently, the degree of ASR in the lower part of the concrete is relatively mild, and it may not form a destructive ASR gel. The unarmful expansion occurring before the ASR gel reaches the point of damaging aggregates and pastes can, to a certain extent, compress the pathways for solution transfer. Additionally, ASR-related cracks might create spaces around the interface between the steel bar and paste, allowing for the storage of corrosion products. It can reduce the stress of the concrete and further impede the penetration of ions. Moreover, the fluid ASR gel covers the surface of the steel bar, serving as insulation against oxygen exposure and preventing the onset of the corrosion reaction (Habuchi et al., 2004). It has been observed when the specimens were cut open, ASR gel was present spreadly in the concrete, and some fluid gels were attached to the surface of the reinforcement. Consequently, the impact of ASR on the corrosion resistance of concrete is very complicated. It not only plays a role on accelerating the initiation of steel corrosion but also prolongs passive steel bars to a certain extent, all depending on the development degree of ASR.

In the concrete case containing fly ash, visible ASR cracks that appear on the surface of FBA concrete are greatly postponed compared with HA. It indicates that the function of pozzolan materials contributes to decrease the ASR degradation to maintain the

surface quality. A higher level of sound concrete appearance helps improving the corrosion resistance of concrete. Besides, the corrosion area on the upper bars of FBA is relieved to a great extent to the HA. Consequently, it could be emphasized that fly ash could mitigate ASR damage as well as the initiation of corrosion and the degree of corrosion propagation. It proves that fly ash also effectively enables delay in the corrosion rate in the concrete confronting ASR threats. Furthermore, the FBA surfaces have no wide longitudinal cracks until the day separating the specimens. Figure 3.11(b) shows that five upper bars have corroded stains, while the middle part of the down bars of FBA4 and FBA5 show corrosion rust and pit holes. As discussed in HA, the ASR in FBA is not necessarily with the opposite effect, while it can also prevent the transport of chloride ions into the concrete and has the function of binding chloride ions. The benefit of unarmful expansion of ASR, retarding the depassivated steel bars, remains to the FBA concretes. Furthermore, the benefit may be escalated in terms of FBA because fly ash can limit the development of ASR.



(a) Upper surface of HA3



(b) Bottom surface of HA3



(c) ASR cracks on the "A" part



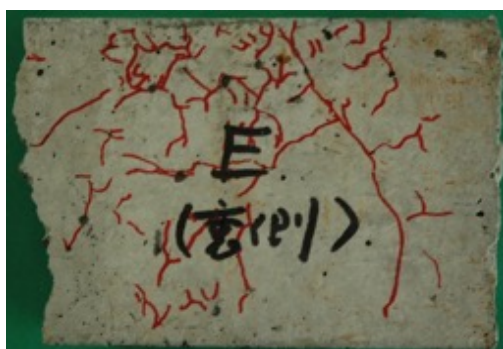
(d) ASR cracks on the "B" part



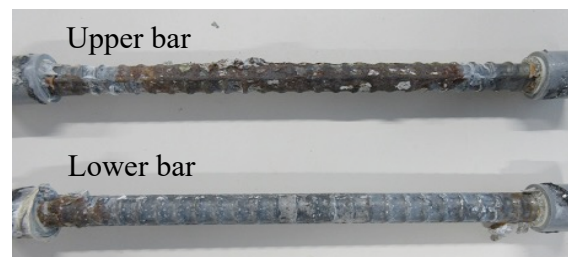
(e) ASR cracks on the "C" part



(f) ASR cracks on the "D" part



(g) ASR cracks on the "E" part



(h) Corroded rebars of HA3

Figure 3.12 ASR cracks on HA3 concrete surface and corroded steel bars at 490 days

3.8 Chloride Resistance of High-early-strength Steam-cured SCMs Concrete

The diffusion of chloride ions in the concrete is associated with chloride-related corrosion resistance. This study selects two sampling locations in each concrete to test the total chloride ion content: 1. The central part of the concrete is where the salt pond is placed, and it abbreviated in “C” afterwards; 2. The second sampling place aims to detect the impact of local chloride ion penetration on the surrounding parts, so the location 5cm away from the outer boundary of the salt pool is selected, and marks as “S”. Figure 3.13 is an example of the sampling locations in concretes. The chloride content measurement has been conducted to obtain chloride profiles of various concrete mixes, and the corresponding apparent chloride ions diffusion coefficient (D_c) and surface chloride concentration (C_0) has been calculated by the best-fitting curve under Fick’s second law. In addition to D_c and C_0 in two parts of concrete, the chloride ion concentrations are around at 3 cm and 7.9 cm, where the upper and lower bars are settled, as shown in Table 17. Estimated values adopts the concentrations in the vicinity of the upper reinforcement and the lower reinforcement. For the chloride ion concentration near the upper steel reinforcement, the raw data is used directly at a distance of depth and 3cm within 2mm; for other cases, the two-point method is used, while the same method applies for the down bar.

Table 17 Total chloride ion concentration at depths around the upper and down bar in five types of concrete

Rebar	Chloride concentration (kg/m^3)									
	H3		HA4		FB5		FBA4		BB5	
	C	S	C	S	C	S	C	S	C	S
Upper	18.6	15.2	18.4	8.7	0.24	0.21	9.93	2.69	7.04	1
Down	9.71	2.47	4.54	0.3	-	-	0.53	0.42	1.43	-

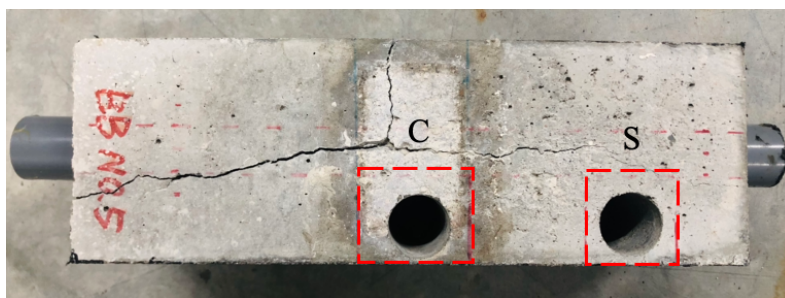


Figure 3.13 Sampling locations for central part (C) and side part (S) for chloride content measurement

3.8.1 Chloride penetration in high-early-strength steam-cured SCMs concrete

1) Chloride profiles and corresponding D_c in Central part of concretes

Figure 3.14 illustrates the chloride profiles of concrete in the central part (C) and the boundary part (S) for selected specimens, namely H3, HA4, FB5, FBA4, BB5, and BB1. In the chloride ion profile "C," it is evident that the curves for all concrete specimens exhibit a declining trend from the concrete surface. However, the degree of decline and the penetration depth vary significantly depending on the concrete type.

For H3 and HA4, the chloride curve slopes are relatively flat, and the distribution of chloride ion concentrations is quite similar. This uniformity may be influenced by the presence of wide longitudinal cracks on the concrete surface. Moreover, given the corrosion location in the down bar of H3 and HA3, it can be inferred that the corrosion cracks initiated in the upper steel bars have propagated downward to deeper positions. HA4 has a higher concentration of chloride ions between the two rebar placements, probably due to the storage of chloride ions in ASR cracks. FBA4 also shows a higher chloride content near the surface, while the chloride ions ingress to the depth decreased significantly. The chloride concentration of FBA4-C at the upper reinforcement is nearly half that of H3 and HA4 and is negligible at the lower bar placement. BB5 and FBA4 have a parallel distribution curve, but the concentration of chloride ions of BB5 at the upper bar is lower, probably because it is not affected by ASR cracks. In other words, FBA4 has a higher chloride ion content than BB5 near the surface depth due to ASR deterioration. However, a corrosion stain occurs on the down rebar of FBA4 where the chloride content is minimal. This phenomenon may prove that the chloride ions can pass along the cracks formed by corroded upper rebar to accumulate on the local area surrounding the down bar. In the FB5 and BB1 specimens without any corrosion, the chloride curves are nearly overlapping and tend to zero before reaching the depth of the upper reinforcement, which is attributed to the contribution of hydrated SCM. The chloride concentration around the surface layer of all concrete has a closer value except for H3, meaning the surface concentration is mainly related to the exposure solution rather than the corrosion degree of the rebars.

Table 18 shows the chloride diffusion coefficients corresponding to the respective chloride profiles in Figure 3.14. The D_c of H3 and HA4 in the central part of the concrete are prominently high, reaching $15.1 \text{ cm}^2/\text{year}$ and $20.0 \text{ cm}^2/\text{year}$, respectively. FBA4 and BB4, the concrete containing SCM but had rebar corrosion show a lower D_c , whereas FB5 and BB1 exhibit extremely low levels. The primary reason for the unusually high D_c revealed by H3 and HA4 is the wide longitudinal cracks, which lead to excess chloride ions entering directly into the cracks and secondary diffusion along the crack walls. The D_c of HA4 confirmed that ASR cracks in HA4 enhanced the diffusion of chloride ions, and a certain concentration of salt solution passing through the active andesite also helped the development of ASR. The vicious circle led chloride ions to diffuse deeply into the concrete, causing the sudden potential drop earlier. Additionally, the degree of ASR in HA concrete varies with the specific location in the

concrete. For example, the total chloride ion content of HA4 at a depth between 3 cm to 7.9 cm is higher than that of other concrete types because the ASR crack provides more space for chloride ions staying. Moreover, the semi-permeable membrane reaction rim formed by calcium alkali silicate absorbs alkaline cations and has a dragging effect on the remaining chloride ions. On the other hand, the decrease in chloride concentration of HA4 after 8 cm may be due to the uneven development of ASR. FBA4 not only has corrosion of steel bars but also the chloride ion diffusion coefficient is vastly times that of FB5 because of plagued by ASR. As a horizontal comparison, the Dc of HA4 is about 1.3 times that of H3, so it can be seen that the influence of ASR cracks on Dc has been neglected by the existence of wide penetrating cracks. The FBA concrete weakens the maximum deformation rate of ASR under the pessimum mix proportion accompanied by the benefits of pozzolanic reaction and the chemical binding capacity of chloride ion of fly ash itself, which makes its Dc less than HA4 by approximately eight times. On the other hand, the Dc of FBA4 and BB5 has no considerable difference, while the corrosion onset time of FBA4 is nearly 300 days earlier than that of BB5, indicating that the correlation between these two parameters may be relatively low. And the reduction of the chloride ion penetration depth of SCMs concrete also means that the pozzolanic reaction inhibits the secondary diffusion of chloride ions in the cracks.

The Dc of FB without any obvious surface damage is nearly 50 times lower than that of H3, the main reason is the absence of wide cracks followed by the excellent chloride ion resistance of fly ash concrete. Besides, by comparing the Dc of H3 with FB5, BB5, and BB1, it can be found that the resistance to chloride ion penetration of blast furnace slag concrete without corrosion cracks is identical to that of fly ash. Moreover, the Dc of BB5 with corrosion cracks is less than nearly seven times that of H3, attributing to that the hydration of blast furnace slag and a retarded corroded time.

2) Chloride profiles and corresponding Dc in the Side part of concretes

Figure 3.14 illustrates the chloride profiles in the side part of the tested concretes. At each depth, H3 exhibits the highest chloride concentration, likely attributable to the extensive longitudinal crack propagation in the side part of H3. In the case of HA4, which displays serious ASR cracks on the concrete surface, its chloride concentration experiences a significant drop at a depth of approximately 4cm. This cannot be solely attributed to longitudinal cracks, as the degree of ASR deterioration varies depending on the concrete's location. Table 17 shows that the chloride concentration of the first layer of FBA4-S concrete reached 20.9 kg/m^3 , indicating that the ASR cracks in FBA4 facilitate the multidirectional transfer of chloride ions from the solution source to the sampling location. The chloride concentration in the first layer of concrete for BB5 is 13.7 kg/m^3 (Table 17), mainly influenced by the presence of longitudinal cracks. In the case of FB5 and BB1, where the concrete surface remains highly intact, there is almost no presence of chloride ions in the S part.

The selected sampling location avoids the position adjacent to the wide crack in order to avoid the influence of the wide crack as much as possible. Figure 3.14 indicates that

the side portions of FB5 and BB1 exhibit minimal chloride penetration. However, the penetration of chloride ions in the concrete specimens with corroded steel bars is still influenced to varying degrees by the presence of corrosion cracks. Note that the chloride diffusion coefficient (D_c) of HA4 is lower than that of H3 in the side part, which could be attributed to the uneven development of ASR. The influence of dynamic ASR development on chloride diffusion in concrete is diverse. Although chloride ions in the surface concrete of FBA4 may transport through the ASR cracks, fly ash (FBA) hinders the diffusion of chloride ions into concrete in the direction of gravity due to the reduced ASR deterioration and pozzolanic reaction. Fly ash preferentially reacts with alkali silicate due to its dimensional advantage (Chappex & Scrivener, 2013), so the presence of high alkali content in ASR gel accelerates the hydration of fly ash particles in concrete. BB5 has secondary D_c due to existing longitudinal cracks on the surface. Contrast, the D_c is minimal because of less chloride content in the surface concrete, which is associated with the absence of microcracks. Chloride penetration in other directions occurred in BB5 due to corrosion cracks, but its excellent optimized dense concrete interior blocked further chloride transport. ASR cracks assist the transfer of chloride ions in the surface concrete and affect the D_c in the concrete that indirectly contacts the salt source.

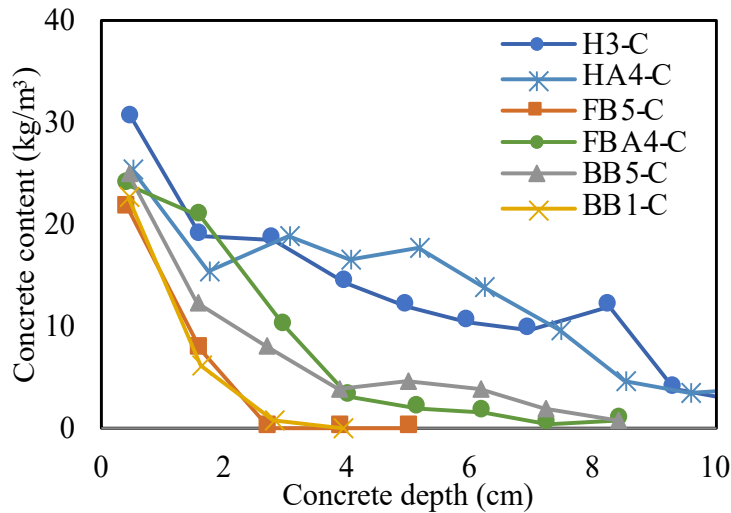
3) Effect of sampling position on Chloride profiles

Comparing the chloride profiles of the central and the side part in HA4 and H3, it conveys that a wide longitudinal crack is a primary factor affecting the distribution of chloride ions. ASR cracks serve as a secondary contributor to chloride penetration, although the extent of ASR deterioration within the same concrete specimen is linked to local concrete conditions. Moreover, the onset of corrosion of lower reinforcements is more closely associated with the infiltration of salt solution along the cracks formed by the corroded upper rebar. This is evident from the significantly low chloride ion content adhering to the lower steel bar.

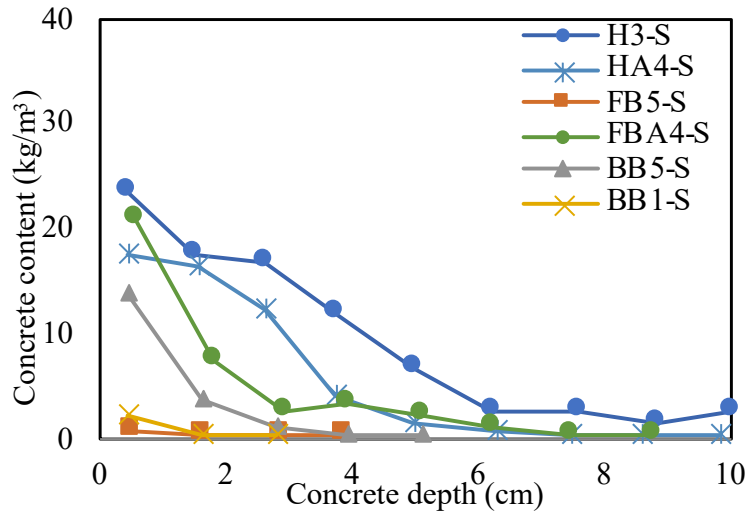
Table 18 Apparent chloride diffusion coefficients (D_c) and chloride surface concentrations (C_0) in central part and side part

Series	Central part		Side part	
	C_0 (kg/m ³)	D_c (cm ² /year)	C_0 (kg/m ³)	D_c (cm ² /year)
H3	27.8	15.1	25.7	6.43
HA4	25.5	20.0	21.2	3.50
FB5	29.4	0.32	- *	
FBA4	29.4	2.50	26.0	0.79
BB5	26.4	2.13	18.8	0.29
BB1	14.7	0.29	- *	

* C_0 and D_c cannot be calculated due to the minimal amount of chloride ingress



(a) Chloride profiles of the central part of concrete



(b) Chloride profiles of the side part of concrete

Figure 3.14 Chloride profiles of five concrete types at (a) central part and (b) side part

3.8.2 Effect of fly ash on steel corrosion resistance of high-early-strength seam-cured concrete under combined damage of ASR and chloride attack

It is well-known that fly ash can inhibit ASR development and enhance the chloride resistance. However, further discussion would like to determine which specific property of fly ash plays a more dominant role in enhancing resistance and prolonging the T_i for upper bar in FBA. Based on the results of accelerated ASR expansion experiments in the most unfavorable 60-degree Celsius environment, HA exhibited significant expansion within the first week, while FBA showed harmful ratio after 15 weeks, which is around 105 days (Figure 3.7). If the 60-degree Celsius environment converts to cumulative temperature for the 40-degree Celsius curing environment, the harmful expansion in FBA occurred 157 days after HA did in the 40-degree environment. In other words, FBA exhibited harmful cracks approximately 150 days after HA in cumulative temperature for the 40-degree Celsius. This time interval closely corresponds to when corrosion began in the upper bars of FBA compared to HA. On

the other hand, it can be observed from Table 15 that the resistivity in upper part of FBA concrete is higher than that of HA nearly 9 times when the upper rebar corroded, respectively. This implies that even though fly ash in FBA significantly enhances the densification compared to HA, when FBA's expansion cracks reach harmful levels, it cannot prevent corrosion. Therefore, ASR resistance may primarily charge the steel corrosion of upper steel bars in FBA. Furthermore, the beneficial effects of fly ash in dense concrete for inhibiting the chloride penetration may have been offset by the deterioration of ASR cracks. This may demonstrate that, the primary mechanism by which fly ash improves the corrosion resistance in FBA is likely by suppressing ASR expansion than the chloride resistance. For concrete HA and FBA that confront threats by ASR, the multiple resistance like chemical attack resistance, physical durability, and corrosion resistance of embedded steel bars are improved simultaneously because of the replacement of fly ash. Additionally, the chloride ions binding capacity of concrete also plays a vital role in hindering chloride-related corrosion. The pozzolanic reaction provides a denser internal structure of the concrete, although not completely exempted but delays the onset of steel corrosion.

FBA concrete effectively reduces the multidirectional transfer and secondary diffusion of chloride ions and protects the steel bars in other intact parts from the harm of corroded steel bars. Although it has been reported that the relatively low pH value of pore solutions in fly ash concrete may lead to reduce the chloride threshold to vulnerable to initiate corrosion (Byfors, 1987), the multiple improvements compensate for this deficiency by pozzolanic reaction in this research. On the other hand, the dispersion of the start time of corrosion of the upper steel reinforcement FBA is 61 days compared to HA's 30 days, which is generally irregular. The previous accelerated length change experiment has proved that fly ash can delay and slow down the deterioration of ASR, and this advantage is also beneficial in the chloride ion exposure experiment. Accordingly, the degree of deterioration of the concrete surface and the diffusion of chloride ions through the internal microcracks of the FBA are lesser than those of HA.

In this study, the corrosion process of the down rebars seems to be difficult to describe only by chloride penetration or ASR damage, because its corrosion initiation (T_i) tends to be affected by the cracking by the corrosion products of upper steel bars. Additionally, ASR in HA and FBA concrete seems to have offered passive protection to the down rebars. Consequently, in HA concrete, the corrosion initiation of the down rebars was extended by almost 478 days compared to that of the upper bars. Furthermore, three down steel bars in FBA concrete did not experience corrosion during the entire three-year experimental duration.

3.9 Summary

This chapter aims to examine the corrosion resistance of steam cured SCMs concrete slabs in deicing salt environment in cold regions. Hence, high-early-strength steam-cured concrete with double-layer steel reinforcement was cast to mimic the application of steel-reinforced concrete bridge slabs, utilizing fly ash (FB) and blast furnace slag (BB) as supplementary cementitious materials with cement replacement ratios of 20% and 50%, respectively. Furthermore, the corrosion resistance of fly ash concrete subjected to the combined damage of chloride penetration and ASR had been studied. Diagnosing the corrosion state of steel bars in high-strength concrete with a thick concrete cover is typically challenging due to the complex internal conditions in the high strength concrete. This study managed to detect corrosion by a unique way via half-cell potential, which was not only provided accurate steel bar information but also fulfilled the service requirements for traffic applications.

1. High strength steam cured concrete incorporating fly ash (FB) and blast furnace slag (BB) exhibited outstanding chloride-related corrosion resistance through improved chloride resistance. The chloride diffusion coefficient (D_c) of concrete added with SCM is minimal. Moreover, FB and BB concrete did not show corroded steel bars for three years subjecting to the exposure environment of 40°C and 10% NaCl solution.
2. This study also confirms that Fly ash addition can effectively delay the development of ASR and hinder the diffusion of chloride ions in steam-cured concrete, thereby delaying the onset of steel corrosion. Moreover, ASR damage can accelerate the corrosion initiation of upper steel bar. However, it appears to offer protection for the lower steel bar by maintaining passivation. Furthermore, the dominant reason affecting the chloride diffusion coefficient is wide cracks, followed by ASR cracks.
3. Half-cell potential method is a highly practical approach for diagnosing steel corrosion in high-strength steam-cured SCM concrete with a thick concrete cover of 7.9 cm. This method facilitates timely corrosion detection while also ensuring the normal traffic services.

CHAPTER 4

CONCLUSIONS AND FUTURE WORKS

4.1 Conclusions

The main conclusions of this research are as follow:

1. Following one year of exposure to cold-region seawater, a calcium-aluminate type admixture of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA2) effectively inhibits chloride penetration in normal-strength steam-cured concrete. This inhibition primarily arises from CA2's high chloride binding capacity, resulting in a reduction of the chloride ion diffusion coefficients (D_c) to 0.53 compared to the N series. Therefore, it indicates that the merely 7 % replacement of OPC is adequate to enhance resistance against chloride penetration in steam-cured concrete.
2. Before seawater exposure, normal-strength steam-cured fly ash concrete exhibited a rough pore structure, while blast furnace slag concrete showed the finest pore structure across three curing methods. Additionally, CA concrete presented comparable pore distribution to N series under the same curing conditions. After one year of seawater exposure in the cold region, steam-cured fly ash concrete (FA) and blast furnace slag concrete (SG) demonstrated a decrease in total porosity, with a redistribution of porosity becoming more concentrated in pore widths smaller than 100nm. Conversely, steam-cured CA concrete exhibited increased porosity with pore sizes larger than 1000nm. However, even with increased porosity in larger pores, steam-cured CA concrete still effectively restricts chloride penetration into the deeper depth.
3. This study indicated that water-binder ratio is the predominant factor than binder types and curing methods that affects the chloride resistance of concrete in the cold seawater. High-strength steam-cured SCM specimens show minimal chloride penetrating into the deep concrete based on the data of one-year seawater exposure. It reveals that the study on chloride resistance of high-strength steam-cured SCMs concrete in marine environment may appreciates an extend experiment duration.
4. This study demonstrated that steel corrosion in high-strength steam-cured SCMs concrete slab with a thick concrete cover can be detected by electrochemical technique of half-cell potential method through a special combination (JB) of reinforcements and the placement of reference electrode. By monitoring the JB potential over time, the corrosion initiation for the upper reinforcement in different types of concrete can be determined. This diagnostic method is not only operable and accurate but also can ensure that the bridge structures in practical applications can perform normal service.
5. The chloride-related corrosion resistance of high-early-strength steam-cured SCMs concrete significantly improved because the pozzolanic reaction and latent cementitious hydration densified the concrete inner structure. Observation experiments on the steel bars were conducted until three years, during which the

steel bars in fly ash concrete and blast furnace slag concrete showed no signs of corrosion and had extremely low chloride diffusion coefficients of $0.32 \text{ cm}^2/\text{year}$ and $0.29 \text{ cm}^2/\text{year}$, respectively, with one exception for blast furnace slag concrete (BB5). Consequently, high-early-strength steam-cured SCMs concrete has promising practical applications as a replacement for damaged concrete bridge slabs in cold regions.

6. In steam-cured concrete threatened by ASR, fly ash not only acts a role to suppress ASR development but also delays chloride-related corrosion of the upper steel bars for nearly twice as long as the control group (HA). Moreover, the uneven development degree of ASR exerted a certain extent in delaying the corrosion of the down steel bar. On the other hand, the influence of ASR cracks on the transport of chloride ions within the concrete is much weaker compared to wide longitudinal cracks. Absolutely, addressing macrocracks promptly is crucial for maintaining the sound condition for reinforced concrete bridges.

4.2 Future Works

1. The chloride ion diffusion phenomenon of concrete in the marine environments in cold regions is affected by multiple factors, and the main influencing factors such as curing method, water-binder ratio, and binder types are discussed in this paper. The complex components in seawater and the weather in field also can affect the chloride ions penetration in long-term, and the research on those aspects are still inadequate. Furthermore, it is challenging to use numerical simulation to simulate the real diffusion of chloride ions in actual seawater exposure in cold regions.
2. $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA2) is a potential additive as a special countermeasure against chloride penetration in concrete. Attractive feature of this particular material is the fact that the amount of the replacement for OPC is merely 7%. Then its handling on a manufacture plant of concrete hardly needs special facilities such as storage tanks. However, the binding mechanism for chloride ions and the phases transition among various hydrated products of CA2 over time subjected to different conditions still requires further study.
3. Corrosion of the upper reinforcement in double-layer reinforced concrete to simulate a bridge slab concrete is well explained in this dissertation through chloride diffusion and the state of the concrete, but it is hard to discuss the same theory for the lower reinforcement. Consequently, it may be possible to reasonably indicate the reasons for the corrosion of the down rebars by combining the knowledge of material mechanics. This requires comprehensive knowledge of concrete to further exploring.

REFERENCES

- Alonso, M. C., & Sanchez, M. Analysis of the variability of chloride threshold values in the literature. *Materials and Corrosion*, 60(8): 631-637.
- Alonso, M. C., Andrade, C., Castellote, M., & Castro, P. (2000). Chloride threshold values to depassivate reinforcing bars embedded in a standardized OPC mortar. *Cement and Concrete research*, 30(7): 1047-1055.
- Andrade, C., & Alonso, M. C. (2004). Test methods for on-site corrosion rate measurement of steel reinforcement in concrete by means of the polarization resistance method. RILEM TC 154-EMC: 'Electrochemical technique for measuring metallic corrosion recommendation. *Materials and Structures*, 37(9): 623-643.
- Angst, U., Elsener, B., Larsen, C. K., & Vennesland, Ø. (2009). Critical chloride content in reinforced concrete—A review. *Cement and concrete research*, 39(12): 1122-1138.
- Angst, U., Elsener, B., Larsen, C. K., & Vennesland, Ø. (2011). Chloride induced reinforcement corrosion: Electrochemical monitoring of initiation stage and chloride threshold values. *Corrosion Science*, 53(4): 1451-1464.
- Assouli, B., Ballivy, G., & Rivard, P. (2008). Influence of environmental parameters on application of standard ASTM C876-91: half-cell potential measurements. *Corrosion Engineering, Science and Technology*, 43(1): 93-96.
- ASTM C876-15. (2015). Standard test method for corrosion potentials of uncoated reinforcing steel in concrete. *ASTM International: West Conshohocken, PA, USA*.
- Atahan, H. N., Oktar, O. N., & Taşdemir, M. A. (2009). Effects of water–cement ratio and curing time on the critical pore width of hardened cement paste. *Construction and Building materials*, 23(3): 1196-1200.
- Azuma, Y., Takewaka, K., Yamaguchi, T., Akira, Y. & Miyaguchi, K. (2017). Immobilization capacity of concrete mixed with $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ as mineral admixture, *Proceedings of JSMS Symposium on Concrete Structure Scenarios*, 17, 357-362.
- Bangert, F., Kuhl D., & Meschke, G. (2004). Chemo-hygro-mechanical modelling and numerical simulation of concrete deterioration caused by alkali-silica reaction. *International Journal for Numerical and Analytical Methods in Geomechanics*, 28(7-8): 689-714.
- Beaudoin, J. J., Ramachandran, V. S., & Feldman, R. F. (1990). Interaction of chloride and C-S-H. *Cement and Concrete Research*, 20(6): 875-883.
- Bensted, J. (2002). Calcium aluminate cements. *Structure and performance of cements*, 2, 114-138.
- Bentur, A. (1980). The pore structure of hydrated cementitious compounds of different chemical composition. *Journal of the American Ceramic Society*, 63(7-8): 381-386.
- Çakır, Ö., & Aköz, F. (2008). Effect of curing conditions on the mortars with and without GGBFS. *Construction and Building Materials*, 22(3): 308-314.
- Cassagnabère, F., Mouret, M., & Escadeillas, G. (2009). Early hydration of clinker–slag–metakaolin combination in steam curing conditions, relation with mechanical properties. *Cement and Concrete Research*, 39(12): 1164-1173.

- Castellano, C. C., Bonavetti, V. L., Donza, H. A., & Irassar, E. F. (2016). The effect of w/b and temperature on the hydration and strength of blastfurnace slag cements. *Construction and Building Materials*, 111, 679-688.
- Chappex, T., & Scrivener, K. L. (2013). The effect of aluminum in solution on the dissolution of amorphous silica and its relation to cementitious systems. *Journal of American Ceramic Society*, 96(2): 592–597.
- Chatterji, S., Thaulow, N., & Jensen, A. D. (1987). Studies of alkali-silica reaction. Part 4. Effect of different alkali salt solutions on expansion. *Cement and Concrete research*, 17(5): 777-783.
- Cheewaket, T., Jaturapitakkul, C., & Chalee, W. (2010). Long term performance of chloride binding capacity in fly ash concrete in a marine environment. *Construction and Building Materials*, 24(8): 1352-1357.
- Cole, W. F., & Hueber, H. V. (1957). Hydrated magnesium silicates and aluminates formed synthetically and by the action of seawater on concrete. *Silicates Industrials*, 22(2): 75-85.
- Cook, R. A., & Hover, K. C. (1999). Mercury Porosimetry of hardened cement pastes. *Cement and Concrete research*, 29(6): 933-943.
- Costa, A., & Appleton, J. (1999). Chloride penetration into concrete in marine environment—Part I: Main parameters affecting chloride penetration. *Materials and Structures*, 32(4): 252-259.
- Cui, L., & Cahyadi, J. H. (2001). Permeability and pore structure of OPC paste. *Cement and Concrete Research*, 31(2): 277-282.
- Dhir, R. K., El-Mohr, M. A. K., & Dyer, T. D. (1996). Chloride binding in GGBS concrete. *Cement and Concrete Research*, 26(12): 1767-1773.
- Dhir, R. K., El-Mohr, M. A. K., & Dyer, T. D. (1997). Developing chloride resisting concrete using PFA. *Cement and Concrete Research*, 27(11): 1633-1639.
- Diamond, S. (1986). Chloride concentrations in concrete pore solutions resulting from calcium and sodium chloride admixtures. *Cement, Concrete, and Aggregates*, 8(2): 97-102.
- Dyer, T. (2014). *Concrete durability*. Crc Press.
- Elsener, B., Andrade C., & Gulikers, J. (2003). Half-cell potential measurements—Potential mapping on reinforced concrete structures. *Materials and Structures*, 36(7): 461-471.
- Enevoldsen, J. N., Hansson, C. M., & Hope, B. B. (1994). The influence of internal relative humidity on the rate of corrosion of steel embedded in concrete and mortar. *Cement and concrete research* 24(7): 1373-1382.
- Escalante-Garcia, J. I., & Sharp, J. H. (1998). Effect of temperature on the hydration of the main clinker phases in Portland cements: Part I, neat cement. *Cement and concrete research*, 28(9): 1245-1257.
- Fernández, R., Ruiz, A. I., & Cuevas, J. (2016). Formation of CASH phases from the interaction between concrete or cement and bentonite. *Clay Minerals*, 51(2): 223-235.

- Fournier B., & Bérubé M. A. (2000). Alkali-aggregate reaction in concrete: a review of basic concepts and engineering implications. *Canadian Journal of Civil Engineering*, 27(2): 167-191.
- Friedmann, H., Amiri, O., & Aït-Mokhtar, A. (2008). Physical modeling of the electrical double layer effects on multispecies ions transport in cement-based materials. *Cement and Concrete Research*, 38(12): 1394-1400.
- Giesche, H. (2006). Mercury Porosimetry: a general (practical) overview. *Particle & particle systems characterization*, 23(1): 9-19
- Glass, G. K., & Buenfeld, N. R. (2000). The influence of chloride binding on the chloride induced corrosion risk in reinforced concrete. *Corrosion Science*, 42(2): 329-344.
- Glasser, F. P. (1991). Chemistry of the alkali-aggregate reaction. *The alkali-silica reaction in concrete*. CRC Press, 30-53.
- Glasser, F. P., Kindness, A., & Stronach, S. A. (1999). Stability and solubility relationships in AFm phases: Part I. Chloride, sulfate and hydroxide. *Cement and Concrete Research*, 29(6): 861-866.
- Glasser, F. P., Marchand, J., & Samson, E. (2008). Durability of concrete—Degradation phenomena involving detrimental chemical reactions. *Cement and Concrete Research*, 38(2): 226-246.
- Gonzalez-Corominas, A., Etxeberria, M., & Poon, C. S. (2016). Influence of steam curing on the pore structures and mechanical properties of fly-ash high performance concrete prepared with recycled aggregates. *Cement and Concrete Composites*, 71, 77-84.
- Gu, P., & Beaudoin, J. J. (1998). Obtaining effective half-cell potential measurements in reinforced concrete structures. *Ottawa: Institute for Research in Construction, National Research Council of Canada*.
- Habuchi, T., Tsuji, H., & Torii, K. (2004). Steel corrosion mechanisms caused by combined action of ASR and chloride penetration. In *Proceedings of Japan Concrete Institute*, 26(1):1017–1022 (in Japanese).
- Halamickova, P., Detwiler, R. J., Bentz, D. P., & Garboczi, E. J. (1995). Water permeability and chloride ion diffusion in Portland cement mortars: relationship to sand content and critical pore diameter. *Cement and concrete research*, 25(4): 790-802.
- Hanif, A., Kim, Y., Lu, Z., & Park, C. (2017). Early-age behavior of recycled aggregate concrete under steam curing regime. *Journal of Cleaner Production*, 152, 103-114.
- Hashimoto, K., Otsuki, N., & Saito, T. (2010). Chemical and physical alteration of cementitious material due to leaching using electrical treatment. *Journal of the Japan Society of Civil Engineers, Ser. E*, 66(4), 520-527. (in Japanese)
- He, Z., Long, G., & Xie, Y. (2012). Influence of subsequent curing on water sorptivity and pore structure of steam-cured concrete. *Journal of Central South University*, 19(4): 1155-1162.
- Heisig, A., Urbonas, L., Beddoe, R. E., & Heinz, D. (2016). Ingress of NaCl in concrete with alkali reactive aggregate: effect on silicon solubility. *Materials and Structures*, 49(10): 4291-4303.

- Hime, W. G. (1996). Delayed ettringite formation-A concern for precast concrete? *PCI journal*, 41(4): 26-30.
- Hoar, T. P., & Jacob, W. R. (1967). Breakdown of passivity of stainless steel by halide ions. *Nature*, 216(5122), 1299-1301.
- Hong, S. Y., & Glasser, F. P. (1999). Alkali binding in cement pastes: Part I. The CSH phase. *Cement and Concrete Research*, 29(12): 1893-1903.
- Hosokawa, Y., Mori, D., Yamada, K., & Yamamoto, M. (2003). EPMA analysis for the determination of apparent diffusion coefficient of chloride ion in concrete. *Cement Science and Concrete Technology*, 57, 293-299.
- Hou, Y. Study on Effect of Steam Curing on Frost damage of Fly Ash Concrete. Master thesis, Hokkaido University. 2017.
- Ichikawa, T. (2009). Alkali-silica reaction, pessimum effects and pozzolanic effect. *Cement and Concrete Research*, 39(8): 716-726.
- Ichikawa, T., & Miura M. (2007). Modified model of alkali-silica reaction. *Cement and Concrete Research*, 37(9): 1291-1297.
- Ito, S., Hori, A., Eki, R., Iyoda, T. (2018). Evaluation of salt resistance concrete using chloride ion immobilized material and expansive additive. *Proceedings of the Japan Concrete Institute*, 40, 729-734. (in Japanese)
- JS Association, JIS A. (2003). 1154: Method of test for chloride ion content in hardened concrete. *Japanese Standards Association*, Tokyo, Japan.
- Kawabata, Y., & Yamada, K. (2017). The mechanism of limited inhibition by fly ash on expansion due to alkali-silica reaction at the pessimum proportion. *Cement and Concrete Research*, 92, 1-15.
- Kawamura, M., & Ichise, M. (1990). Characteristics of alkali-silica reaction in the presence of sodium and calcium chloride. *Cement and Concrete Research*, 20(5): 757-766.
- Kayali O., Khan M. S. H., & Ahmed M. S. (2012). The role of hydrotalcite in chloride binding and corrosion protection in concretes with ground granulated blast furnace slag. *Cement and Concrete Composites*, 34(8): 936-945.
- Khan, M. U., Ahmad, S., & Al-Gahtani, H. J. (2017). Chloride-induced corrosion of steel in concrete: an overview on chloride diffusion and prediction of corrosion initiation time. *International journal of corrosion*, 2017.
- Kimura, Y., Watanabe, H., & Nakamura, E. Maintenance of Concrete Bridges Deteriorated by Chloride Attack in Japan.
- Kjellsen, K. O., Detwiler, R. J., & Gjrv, O. E. (1991). Development of microstructures in plain cement pastes hydrated at different temperatures. *Cement and Concrete Research*, 21(1): 179-189.
- Kumar, R., & Bhattacharjee, B. (2003). Porosity, pore size distribution and in situ strength of concrete. *Cement and concrete research*, 33(1), 155-164.
- L'Hpital, E., Lothenbach, B., Kulik, D. A., & Scrivener, K. (2016). Influence of calcium to silica ratio on aluminium uptake in calcium silicate hydrate. *Cement and Concrete Research*, 85, 111-121.

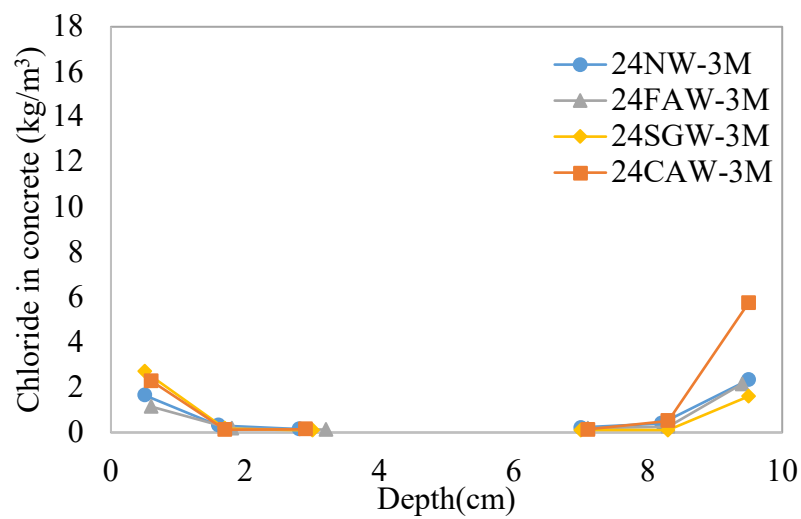
- Laskar, M. A. I., Kumar, R., & Bhattacharjee, B. (1997). Some aspects of evaluation of concrete through mercury intrusion porosimetry. *Cement and Concrete Research*, 27(1): 93-105.
- Lawrence, P., Cyr M., & Ringot, E. (2003). Mineral admixtures in mortars: effect of inert materials on short-term hydration. *Cement and Concrete Research*, 33(12): 1939-1947.
- Lee, Y., Kim, M., Chen, Z., Lee, H., & Lim, S. (2018). Chloride-Binding capacity of Portland cement paste blended with synthesized CA_2 ($CaO \cdot 2Al_2O_3$). *Advances in Materials Science and Engineering*, 2018.
- Li, C., Jiang, L., Xu, N., & Jiang, S. (2018). Pore structure and permeability of concrete with a high volume of limestone powder addition. *Powder Technology*, 338, 416-424.
- Luping, T. (2003). *Chloride ingress in concrete exposed to marine environment-field data up to 10 years exposure*.
- Luping, T., & Nilsson, L. O. (1993). Chloride binding capacity and binding isotherms of OPC pastes and mortars. *Cement and Concrete Research*, 23(2): 247-253.
- Mehta, P. K., & Monteiro, P. J. (2014). *Concrete: microstructure, properties, and materials*. McGraw-Hill Education.
- Miyawaki, M., Ito, S., & Iyoda, T. (2021). Evaluation of Salt Resistance by Different Mix Proportion on Concrete Using Expansive Materials and Calcium Aluminate Admixture. In *The 9th International Conference of Asian Concrete Federation (ACR202/2021)*, 2021, 65-71.
- Monteiro, P. J. M., Wang, K., Sposito, G., Dos Santos, M. C., & de Andrade, W. P.I. (1997). Influence of mineral admixtures on the alkali-aggregate reaction. *Cement and Concrete Research*, 27(12): 1899-1909.
- Mori, D., & Yamada, K. (2007). A review of recent applications of EPMA to evaluate the durability of concrete. *Journal of Advanced Concrete Technology*, 5(3): 285-298.
- Mori, D., Yamada, K., Hosokawa, Y., & Yamamoto, M. (2006). Applications of electron probe microanalyzer for measurement of Cl concentration profile in concrete. *Journal of Advanced Concrete Technology*, 4(3): 369-383.
- Mori, N., Kato, N., & Morita, M. (2017, May). Automatic processing of element maps by automatic colour map filter and high speed cluster analyses for EPMA. In *EMAS 2017 Conference abstract. Konstanz, Germany*.
- Morioka, S., Tahara, K., Yamamoto, K., & Araki, A. (2010). The inhibitory effect and mechanism of $CaO \cdot 2Al_2O_3$ on chloride ion diffusion. In Concrete Technology Series No. 89 of the Japan Concrete Institute: Study on Property Changes and Performance Evaluation of Concrete Using Blended Materials (Report of Committee 333), (No. 2), 443-448. (in Japanese)
- Narmluk, M., & Nawa, T. (2011). Effect of fly ash on the kinetics of Portland cement hydration at different curing temperatures. *Cement and Concrete Research*, 41(6): 579-589.
- Nedunuri, S., Sertse S., & Muhammad, S. (2020). Microstructural study of Portland cement partially replaced with fly ash, ground granulated blast furnace slag and silica fume as determined by pozzolanic activity. *Construction and Building Materials*, 238, 117561.

- Nguyen, P. T., & Amiri, O. (2014). Study of electrical double layer effect on chloride transport in unsaturated concrete. *Construction and Building Materials*, 50, 492-498.
- Otieno, M., Beushausen, H., & Alexander, M. (2016). Chloride-induced corrosion of steel in cracked concrete—Part I: Experimental studies under accelerated and natural marine environments. *Cement and Concrete Research*, 79, 373-385.
- Poon, C. S., Lam, L., & Wong, Y. L. (1999). Effects of fly ash and silica fume on interfacial porosity of concrete. *Journal of Materials in Civil Engineering*, 11(3): 197-205.
- Poon, C. S., Lam, L., & Wong, Y. L. (2000). A study on high strength concrete prepared with large volumes of low calcium fly ash. *Cement and Concrete Research*, 30(3): 447-455.
- Qu, F., Li, W., Dong, W., Tam, V. W., & Yu, T. (2021). Durability deterioration of concrete under marine environment from material to structure: A critical review. *Journal of Building Engineering*, 35, 102074.
- Ragab, A. M., Elgammal, M. A., Hodhod, O. A., & Ahmed, T. E. (2016). Evaluation of field concrete deterioration under real conditions of seawater attack. *Construction and Building Materials*, 119, 130-144.
- Ramezaniapour, A., & Malhotra, V. (1995). Effect of curing on the compressive strength, resistance to chloride-ion penetration and porosity of concretes incorporating slag, fly ash or silica fume. *Cement and Concrete Composites*, 17(2): 125-133.
- Rodriguez, P., E. Ramirez, & Gonzalez, J. A. (1994). Methods for studying corrosion in reinforced concrete. *Magazine of Concrete Research*, 46(167): 81-90.
- Scrivener, K. L., Cabiron, J. L., & Letourneux, R. (1999). High-performance concretes from calcium aluminate cements. *Cement and Concrete Research*, 29(8): 1215-1223.
- Shi Z., Geiker, M. R., De Weerd, K., Østnor, T. A., Lothenbach, B., Winnefeld, F., & Skibsted, J. (2017). Role of calcium on chloride binding in hydrated Portland cement–metakaolin–limestone blends. *Cement and Concrete Research*, 95, 205-216.
- Shi, X., Xie, N., & Fortune, K. (2012). Durability of steel reinforced concrete in chloride environments: An overview. *Construction and Building Materials*, 30, 125-138.
- Sorrentino, F. (1995). Mechanisms of hydration of calcium aluminate cements. *Materials Science of Concrete*, 6, 41-90.
- Stratmann, M. (1990). The atmospheric corrosion of iron—a discussion of the physico-chemical fundamentals of this omnipresent corrosion process invited review. *Berichte der Bunsengesellschaft für physikalische Chemie*, 94(6), 626-639.
- Sugiyama, T., Ritthichauy W., & Tsuji Y. (2008). Experimental investigation and numerical modeling of chloride penetration and calcium dissolution in saturated concrete. *Cement and Concrete Research*, 38(1): 49-67.
- Suryavanshi, A. K., & Swamy, R. N. (1996). Stability of Friedel's salt in carbonated concrete structural elements. *Cement and Concrete Research*, 26(5): 729-741.
- Suryavanshi, A. K., Scantlebury, J. D., & Lyon, S. B. (1996). Mechanism of Friedel's salt formation in cements rich in tri-calcium aluminate. *Cement and Concrete Research*, 26(5): 717-727

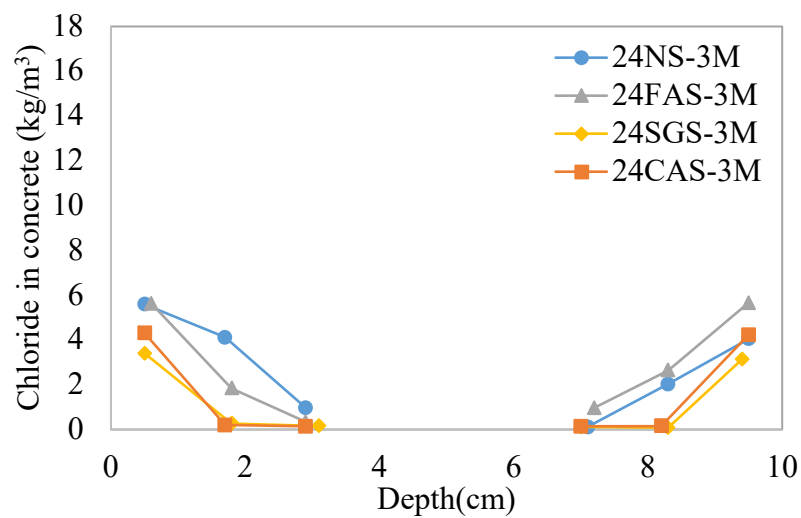
- Tabara, K., Yamamoto, K., Ashida, M., & Morioka, M. (2013). Fixation ability of chloride ion by hardened cement added with $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$. *Cement science and concrete technology*, 66(1), 491-498.
- Tabara, K., Yamamoto, K., Ashida, K., & Morioka, S. (2010). Chloride ion fixation performance in cement hydrates incorporating $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$. *Journal of the Cement and Concrete Association*, No. 64, 428-434. (in Japanese)
- Tanaka, Y., Ishida, T., Iwaki, I. & Sato, K. (2017). Multiple protection design for durable concrete bridge deck in cold regions. *Journal of JSCE*, 5(1): 68-77.
- Thomas, M. D. A. (2011). The effect of supplementary cementing materials on alkali-silica reaction: A review. *Cement and Concrete Research*, 41(12): 1224-1231.
- Toyofuku, T., Takahashi, N., Nagamatsu, T., & Hosokawa, T. (2015). Development of Non-destructive methods for testing the air permeability and water permeability of surface concrete using double chamber method. *Annual Journal of Concrete Engineering*, 37(1), 1801-1806. (in Japanese)
- Ueda, T., Kushida J., Tsukagoshi, M., & Nanasawa, A. (2014). Influence of temperature on electrochemical remedial measures and complex deterioration due to chloride attack and ASR. *Construction and Building Materials*, 67, 81-87.
- Ukrainczyk, N., & Matusinović, T. (2010). Thermal properties of hydrating calcium aluminate cement pastes. *Cement and Concrete Research*, 40(1): 128-136.
- Wang, N., & Sugiyama, T. (2023). Corrosion evaluation of steel bars in steam-cured concrete under chloride attack and alkali-silica reaction. *Magazine of Concrete Research*, 75(9), 433-446.
- Wang, N., Cahyadi, A., & Sugiyama, T. (2021). Corrosion evaluation of steel reinforcement embedded in steam cured high strength concrete slab with electrochemical technique. In *Bridge Maintenance, Safety, Management, Life-Cycle Sustainability and Innovations*, 4137-4143. CRC Press.
- Washburn, E. W. (1921). Note on a method of determining the distribution of pore sizes in a porous material. *Proceedings of the National Academy of Sciences*, 7(4): 115-116.
- Winslow, D. N., Cohen, M. D., Bentz, D. P., Snyder, K. A., & Garboczi, E. J. (1994). Percolation and pore structure in mortars and concrete. *Cement and Concrete Research*, 24(1), 25-37.
- Yamada, K., Tanaka, A., Oda, S., Sagawa, Y., Ogawa, S., & Ochiai, T. (2016). Exact effects of temperature increase and alkali boosting in concrete prism tests with alkali wrapping. In *Proceedings of 14th International Conference on Alkali-Aggregate Reaction* (Vol. 203).
- Yang, K., Basheer, P. A. M., Bai, Y., Magee, B. J., & Long, A. E. (2014). Development of a new in situ test method to measure the air permeability of high-performance concretes. *NDT & E International*, 64, 30-40.
- Yazıcı, H., Aydın, S., Yiğiter, H., & Baradan, B. (2005). Effect of steam curing on class C high-volume fly ash concrete mixtures. *Cement and Concrete Research*, 35(6), 1122-1127.
- Yazıcı, H., Yardımcı, M. Y., Yiğiter, H., Aydın, S., & Türkel, S. (2010). Mechanical properties of reactive powder concrete containing high volumes of ground granulated blast furnace slag. *Cement and Concrete Composites*, 32(8), 639-648.

- Ye, G. (2005). Percolation of capillary pores in hardening cement pastes. *Cement and Concrete Research*, 35(1), 167-176.
- Yokota, M. (1999). Study on corrosion monitoring of reinforcing steel bars in 36-year-old actual concrete structures. *Concrete Library of JSCE*, 33, 155-164.
- Zain, M. M., & Radin, S. S. (2000). Physical properties of high-performance concrete with admixtures exposed to a medium temperature range 20° C to 50° C. *Cement and Concrete Research*, 30(8), 1283-1287.
- Zeyad, A. M., Tayeh, B. A., Adesina, A., de Azevedo, A. R., Amin, M., Hadzima-Nyarko, M., & Agwa, I. S. (2022). Review on effect of steam curing on behavior of concrete. *Cleaner Materials*, 3, 100042.
- Zibara, H., (2001). *Binding of external chlorides by cement pastes* (Doctoral dissertation).

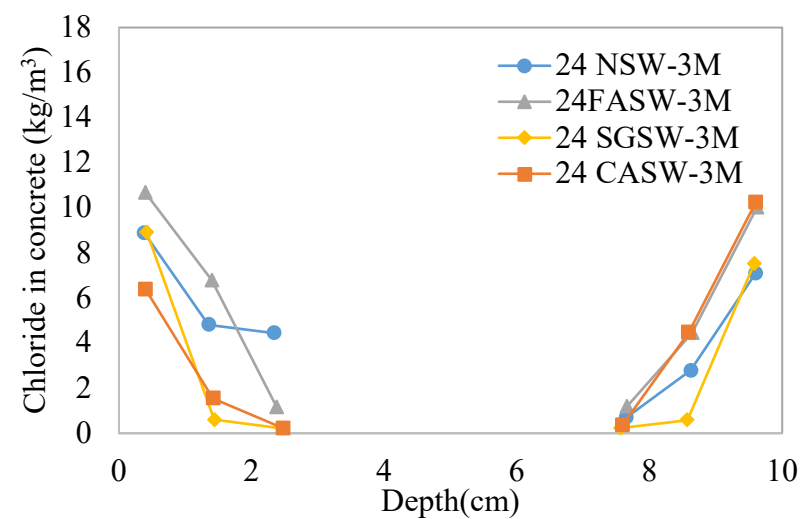
APPENDIX A



(a) 24W-3M series

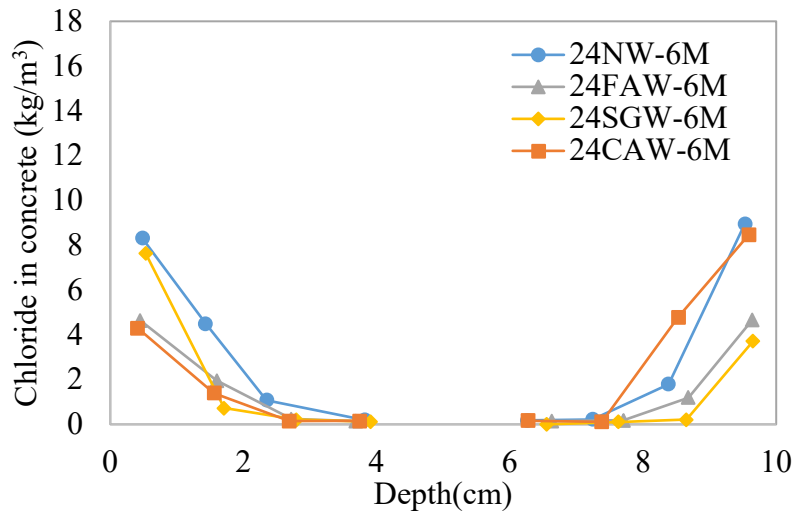


(b) 24S-3M series

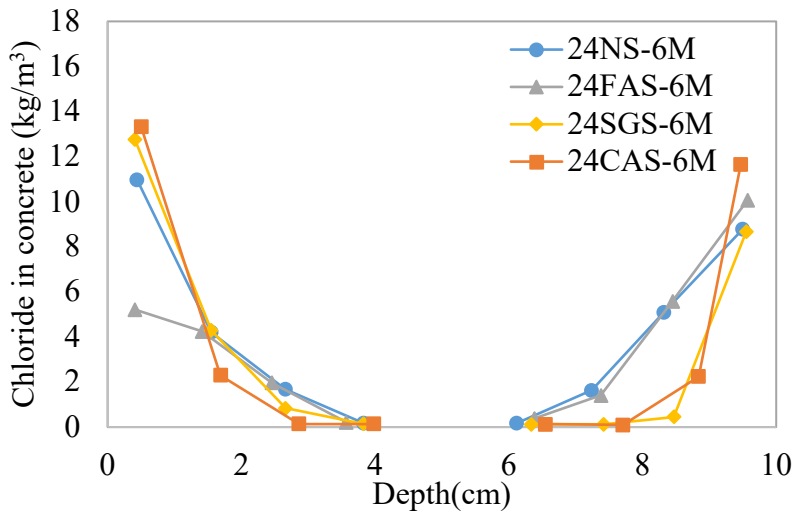


(c) 24SW-3M series

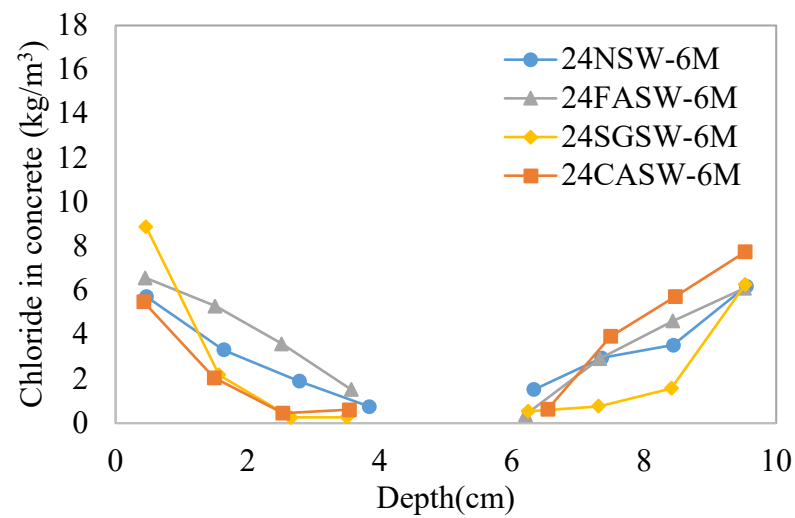
APPENDIX A(1) Chloride profiles of 24 series at three months



(a) 24W-6M series

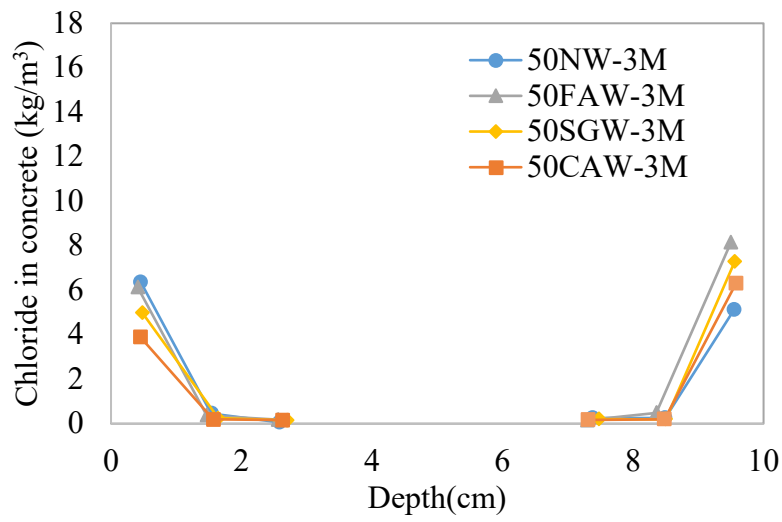


(b) 24S-6M series

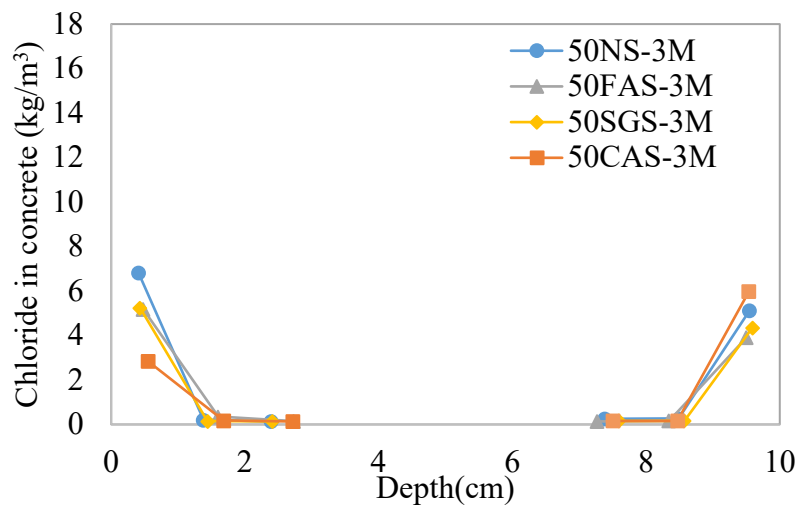


(c) 24SW-6M series

APPENDIX A(2) Chloride profiles of 24 series at six months

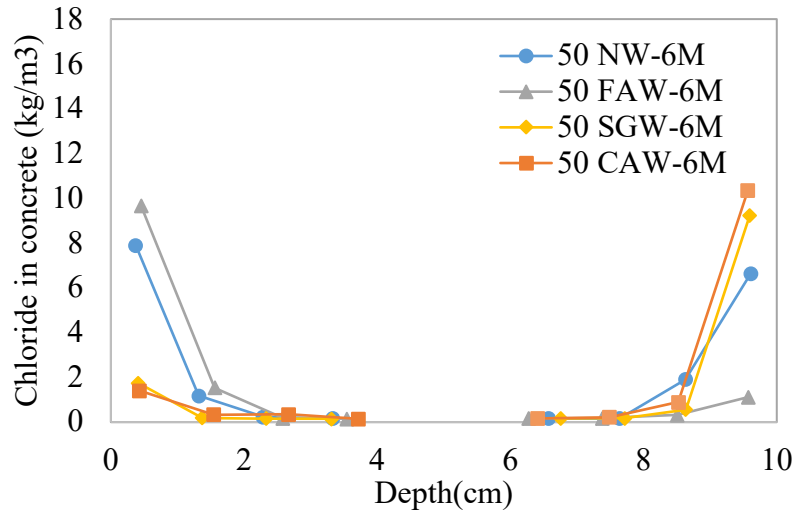


(a) 50W-3M series

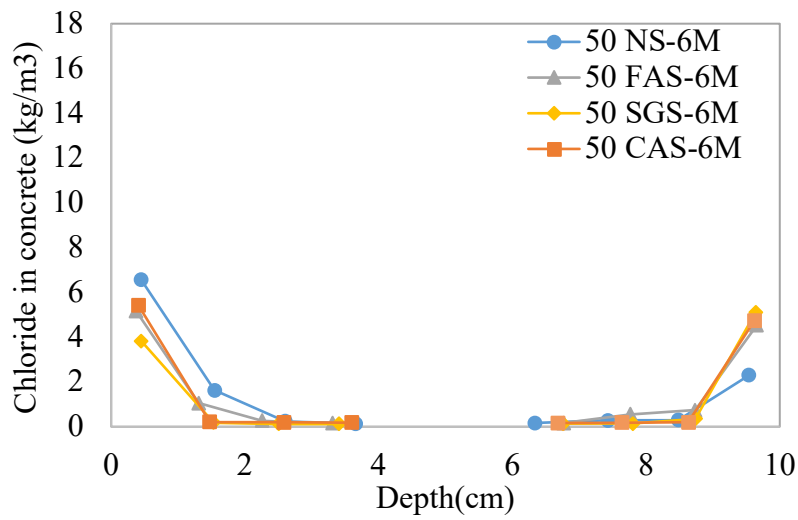


(b) 50S-3M series

APPENDIX A(3) Chloride profiles of 50 series at three months



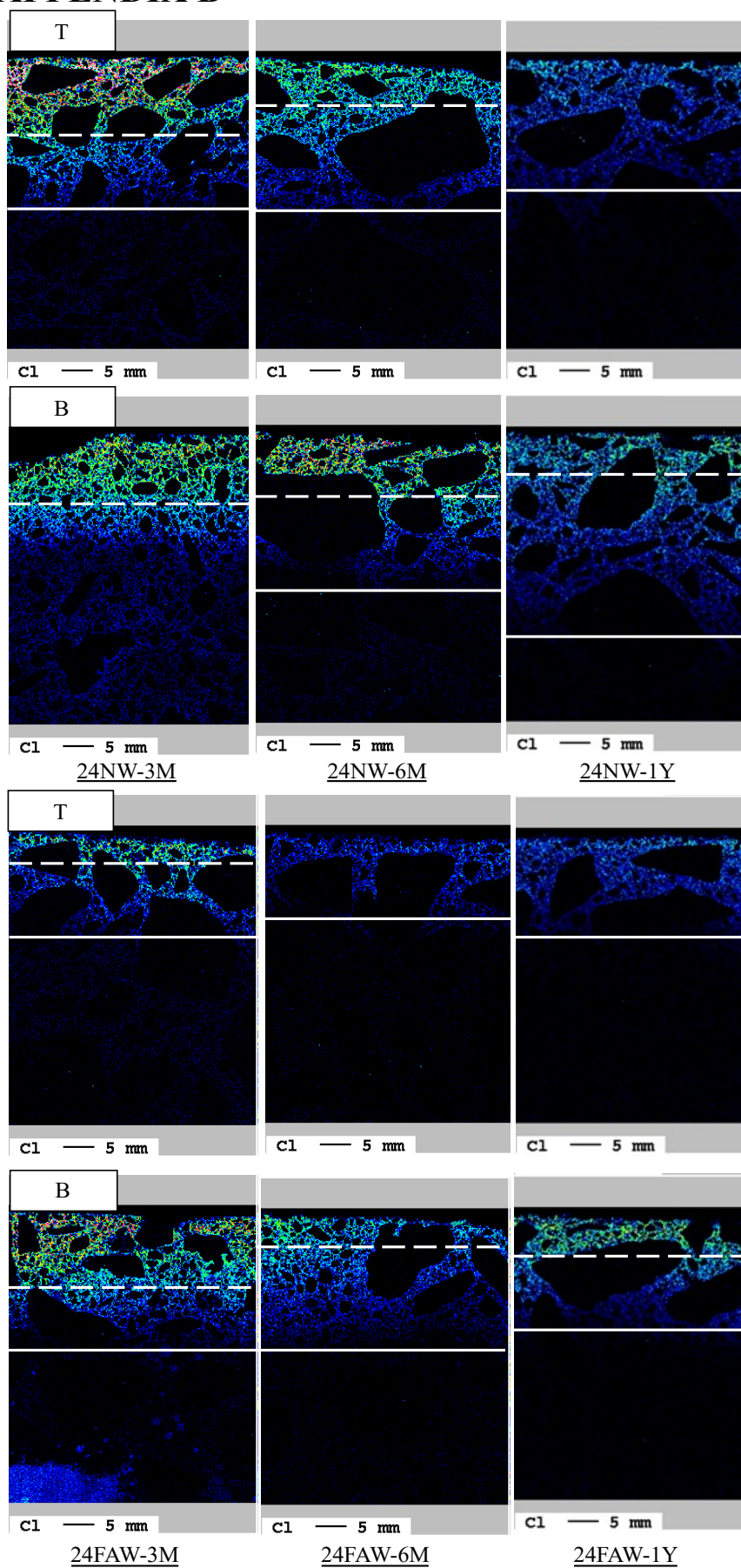
(a) 50W-6M series

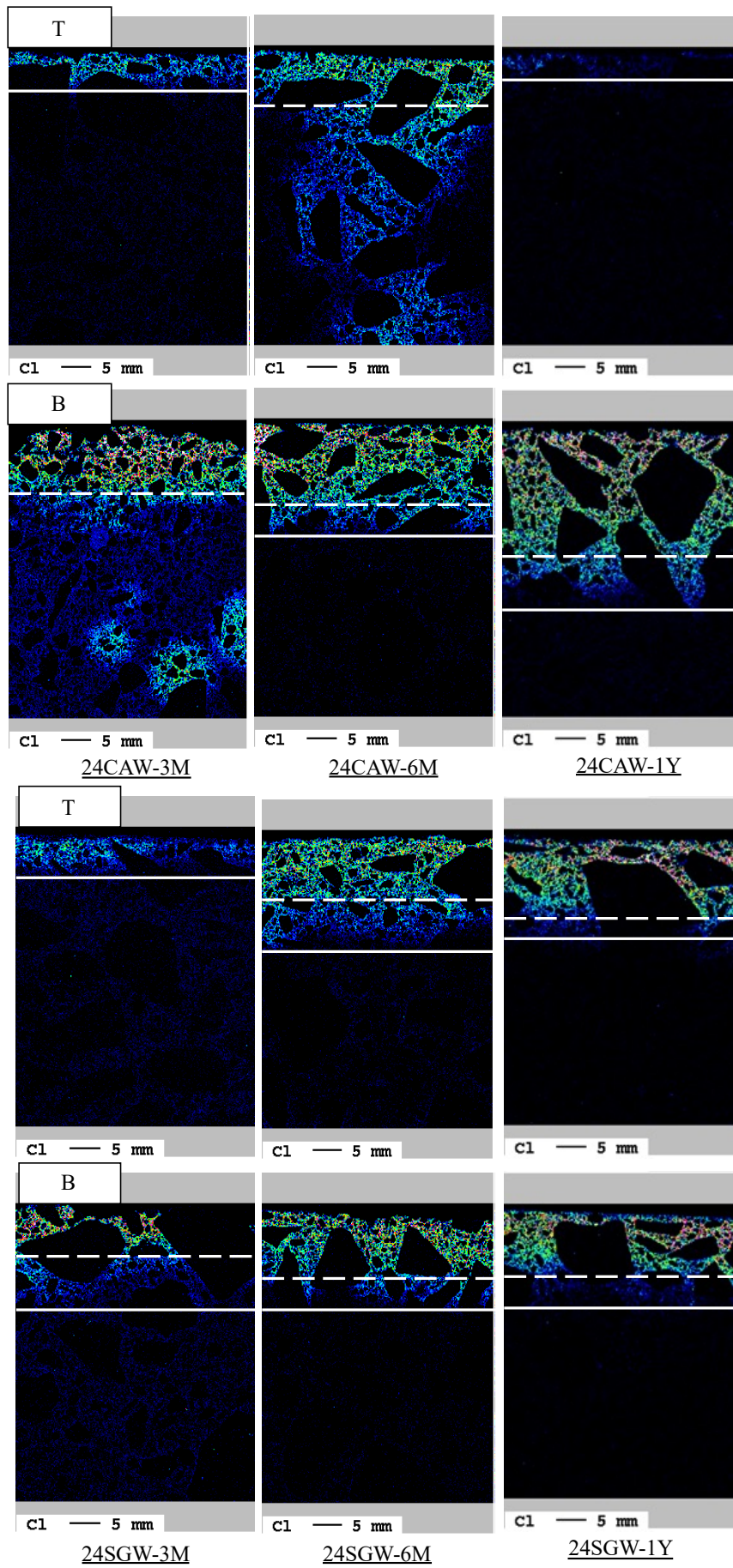


(b) 50S-6M series

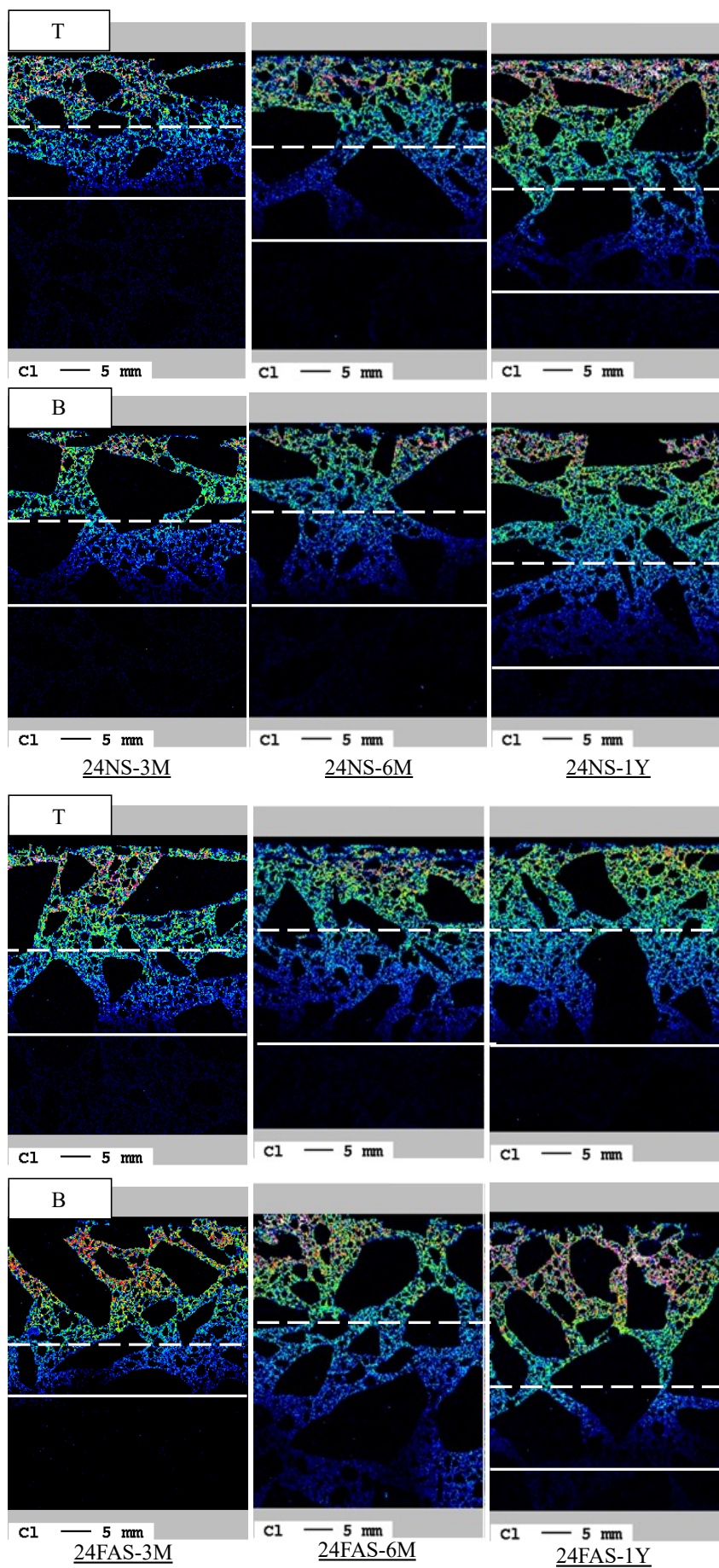
APPENDIX A(4) Chloride profiles of 50 series at six months

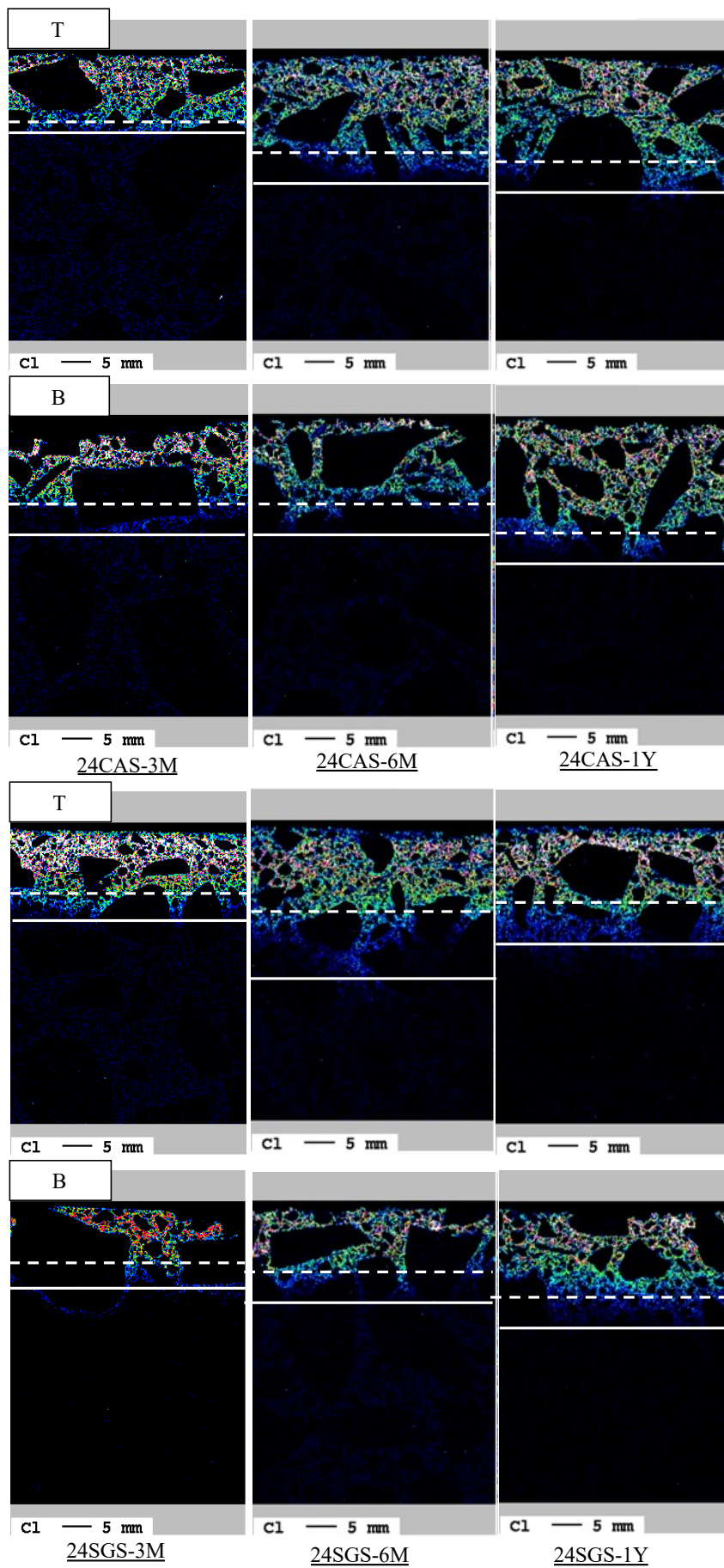
APPENDIX B



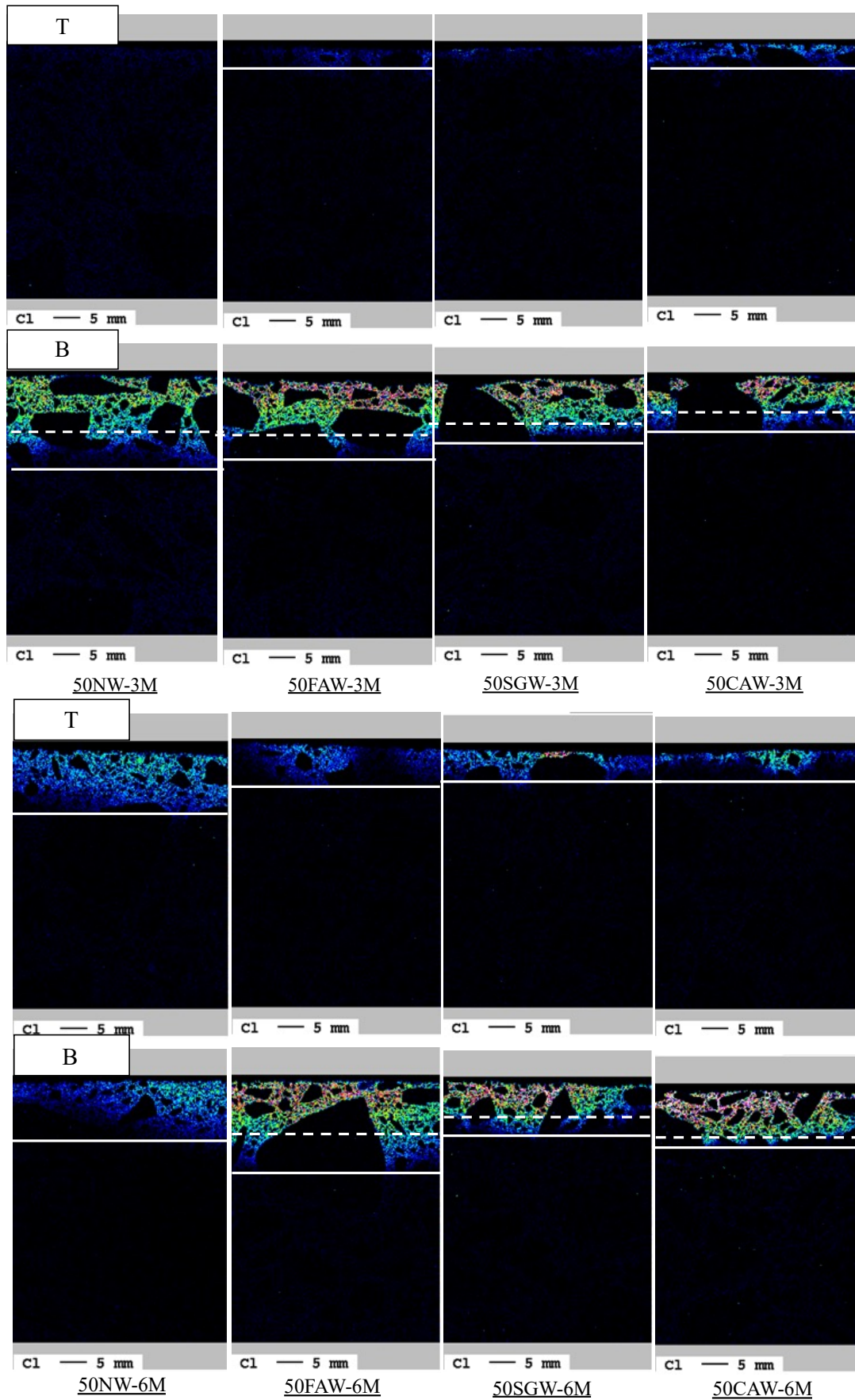


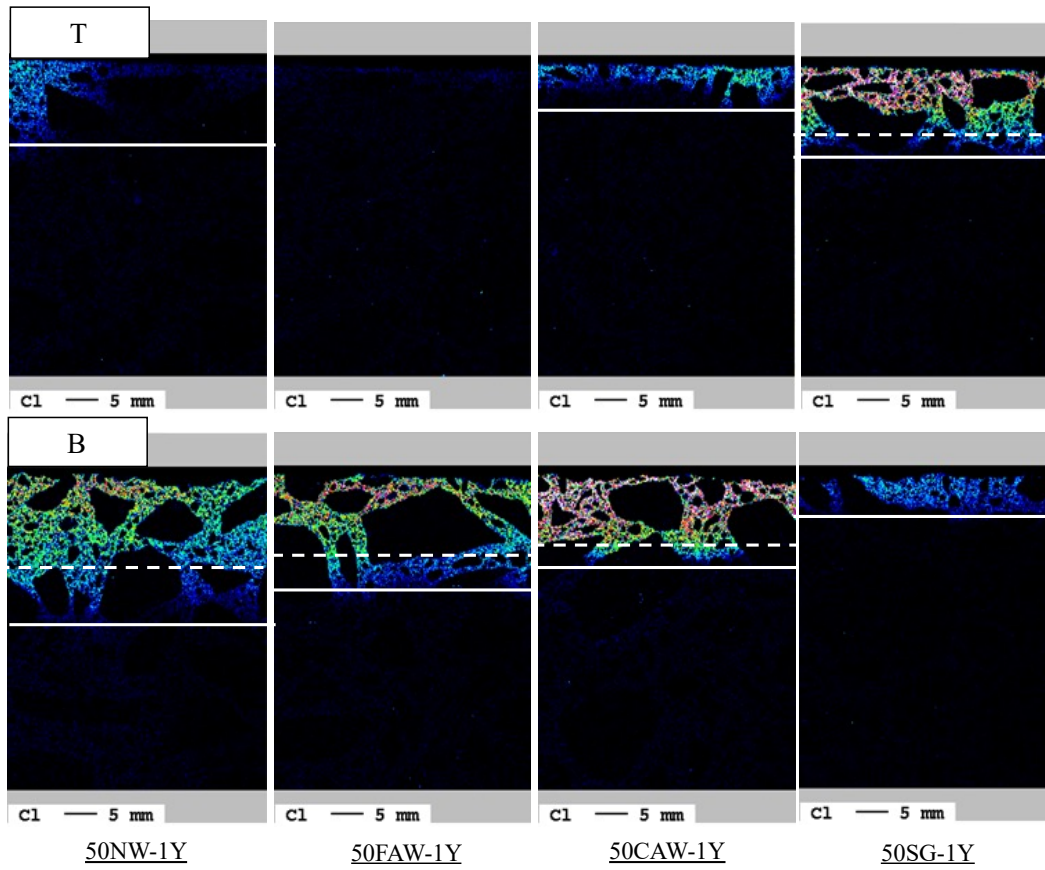
Appendix B(1) EPMA images of the 24W series over one year



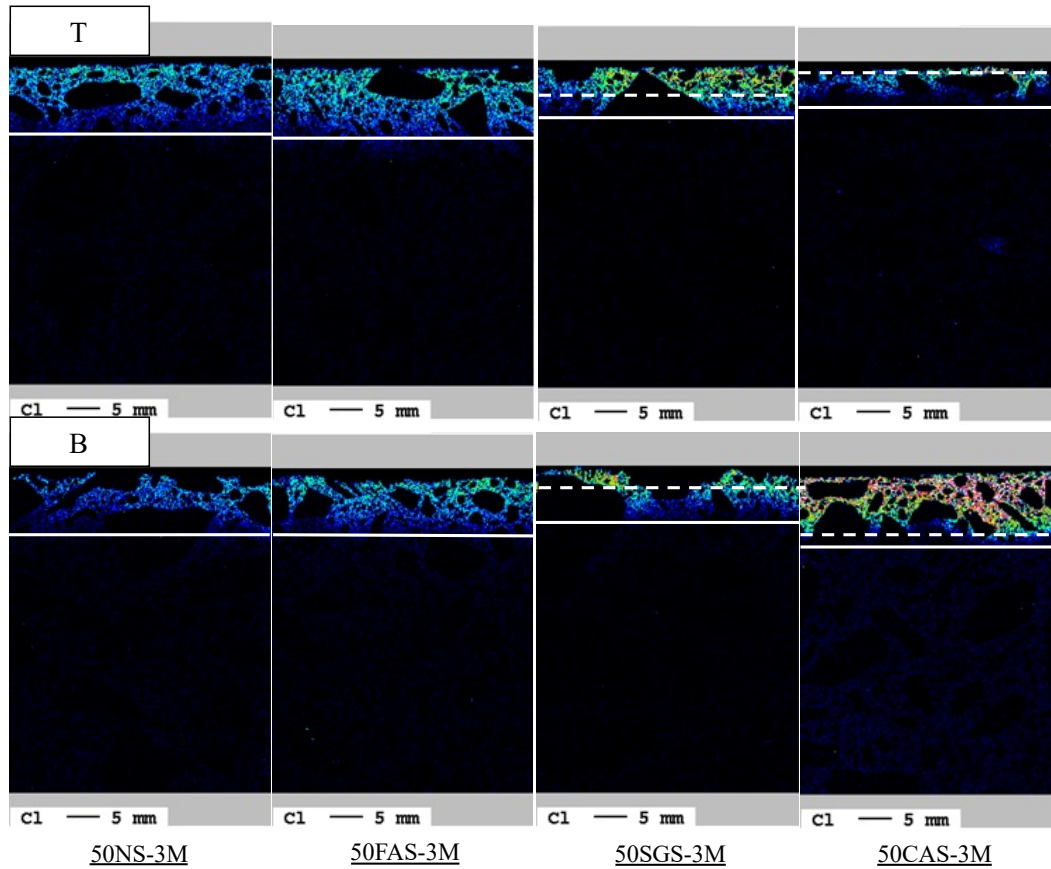


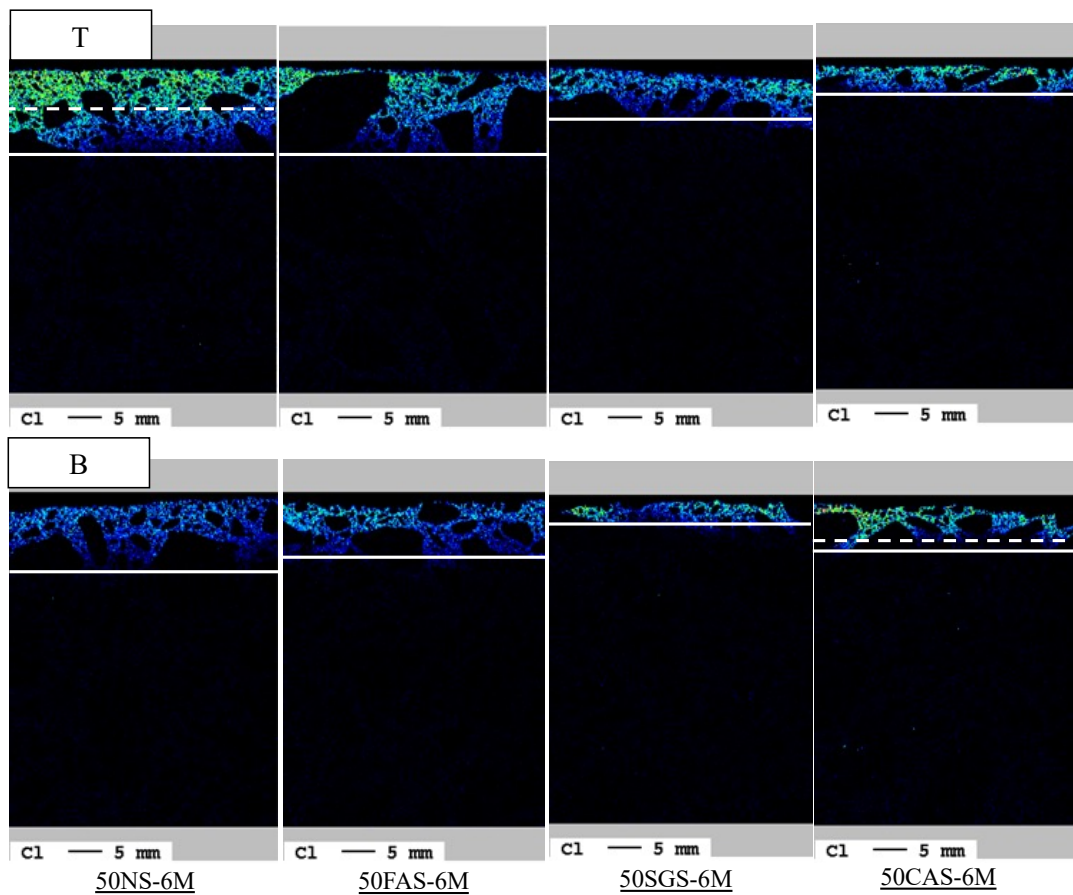
Appendix B(2) EPMA images of the 24S series over one year



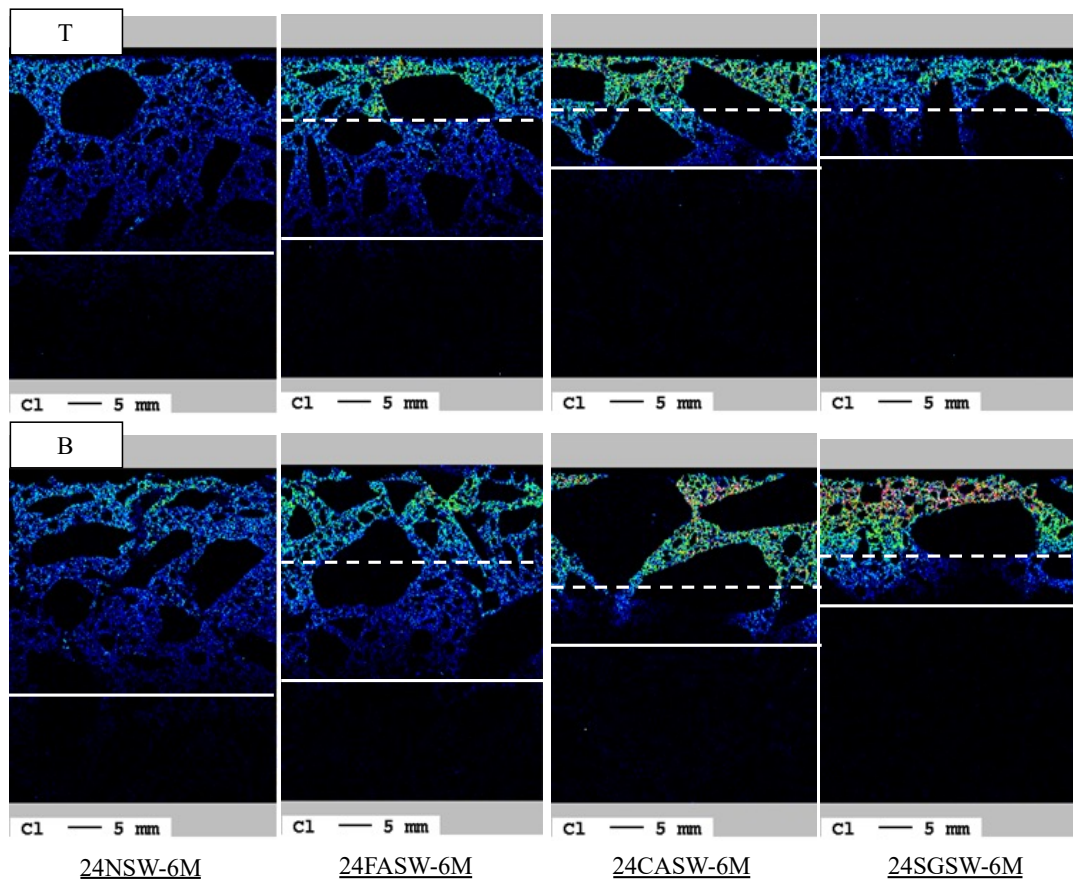


Appendix B(3) EPMA images of the 50W series over one year

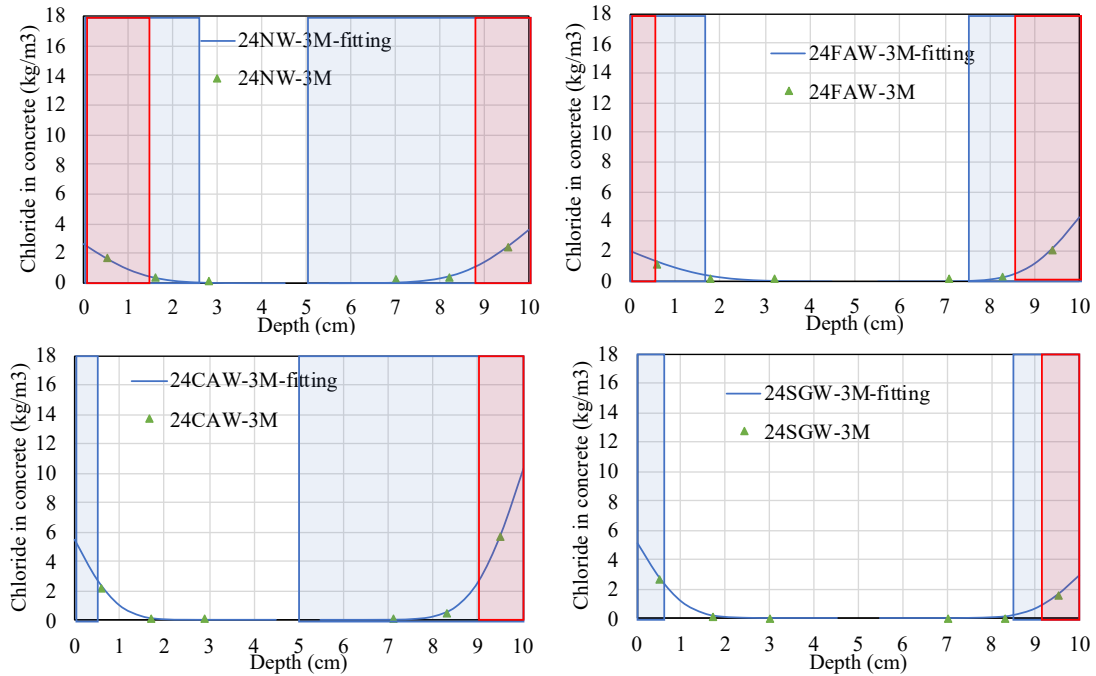




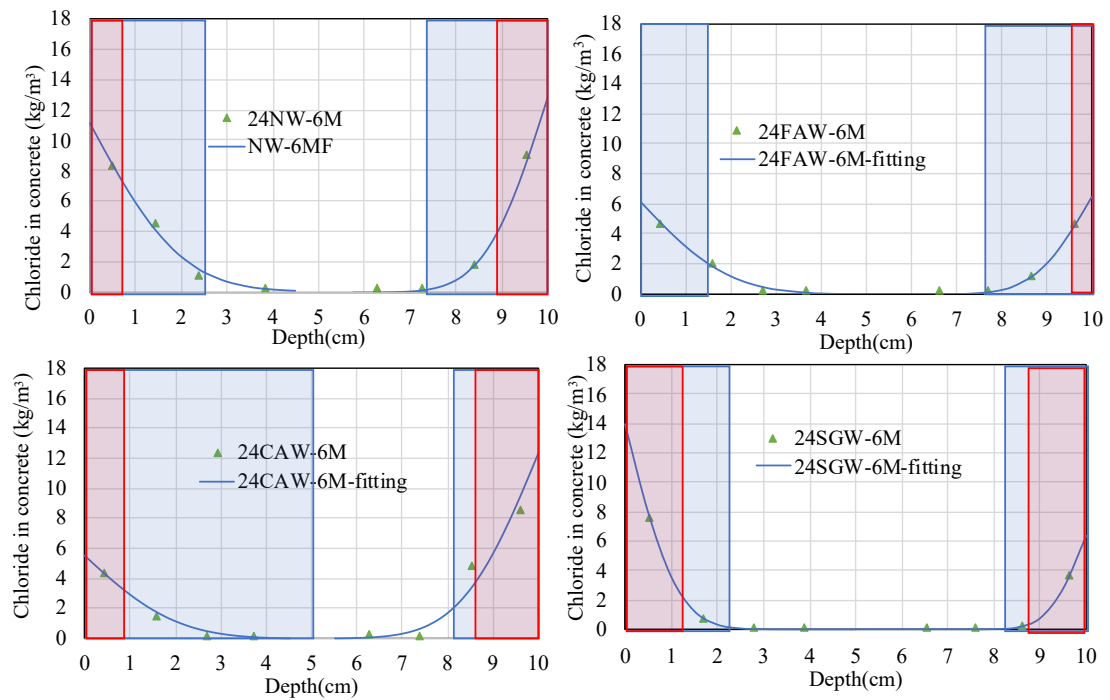
Appendix B(4) EPMA images of the 50S series at three months and six months



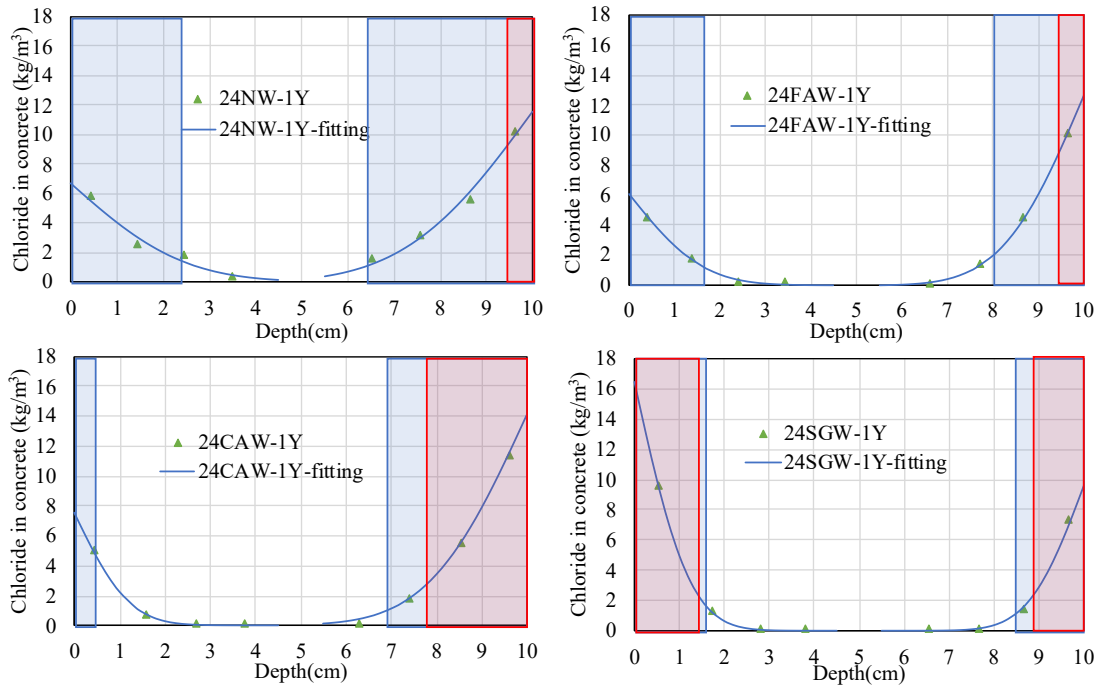
APPENDIX C



(a) Fitting curves of the 24W series at three months

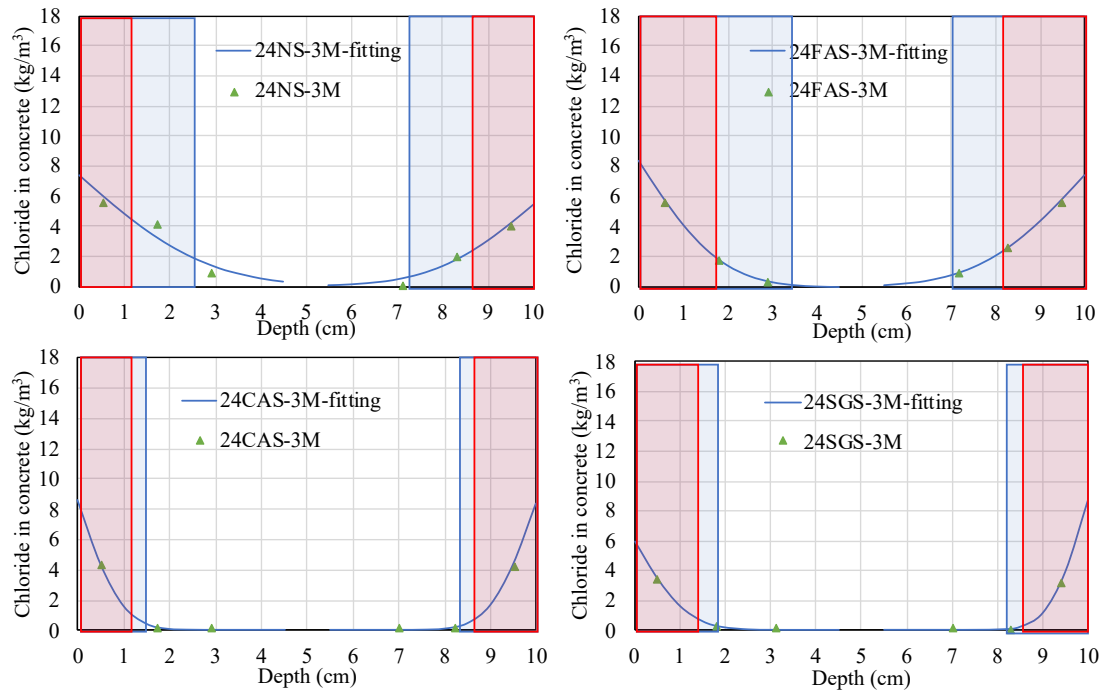


(b) Fitting curves of the 24W series at six months

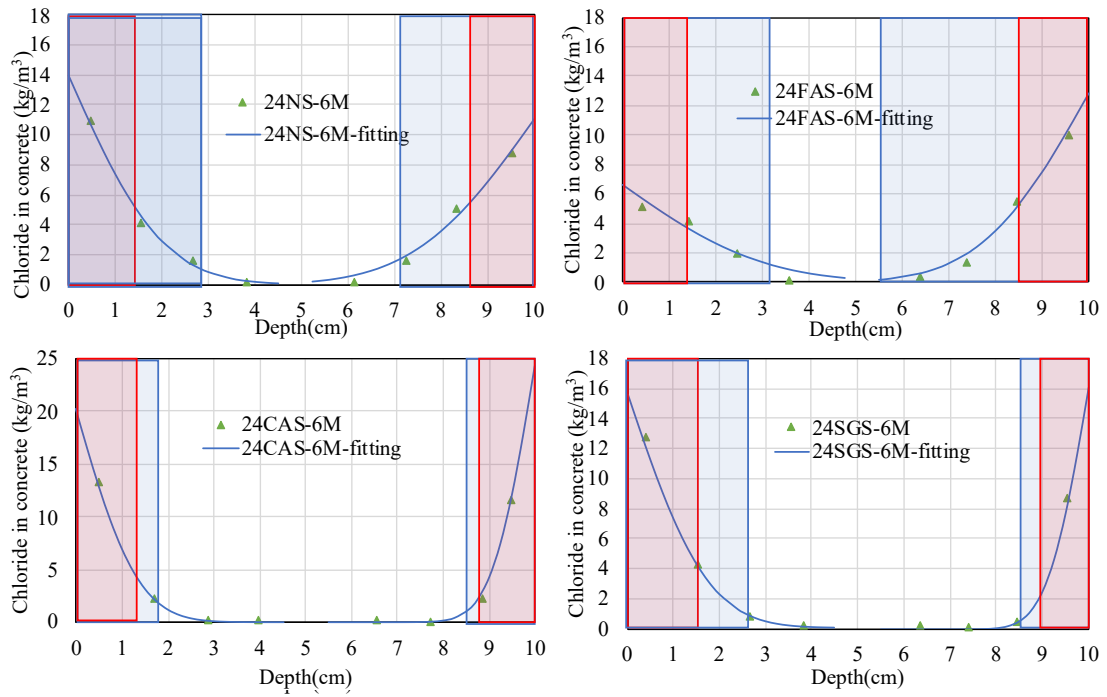


(c) Fitting curves of the 24W series at one year

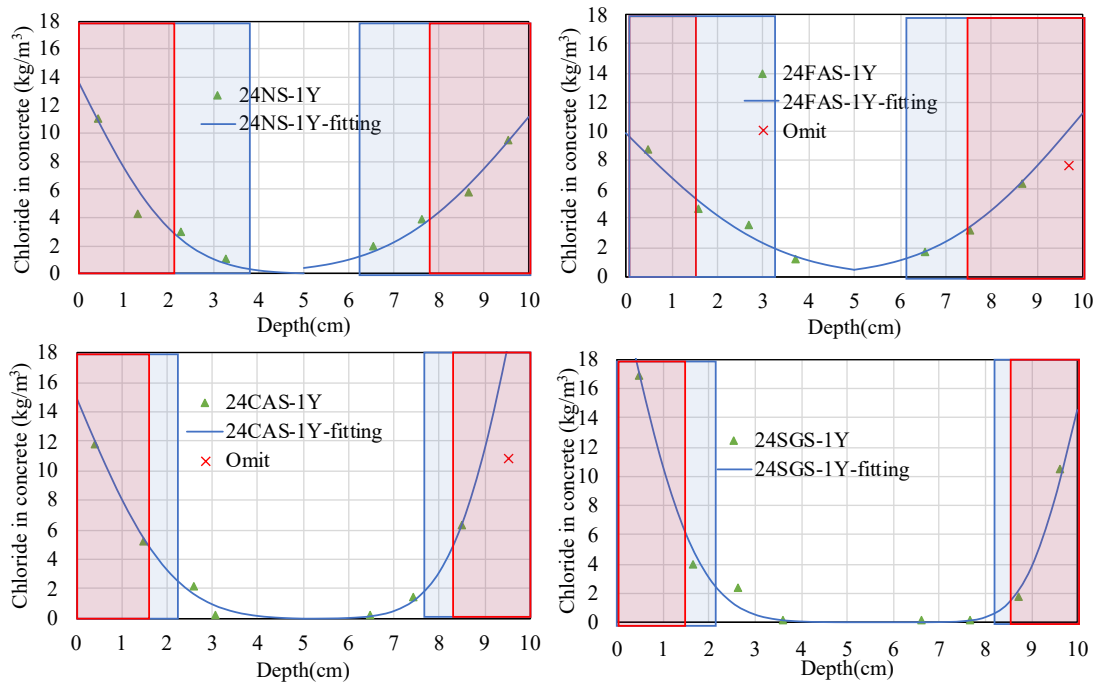
Appendix C (1) Fitting curves of the 24W series over one year



(a) Fitting curves of the 24S series at three months

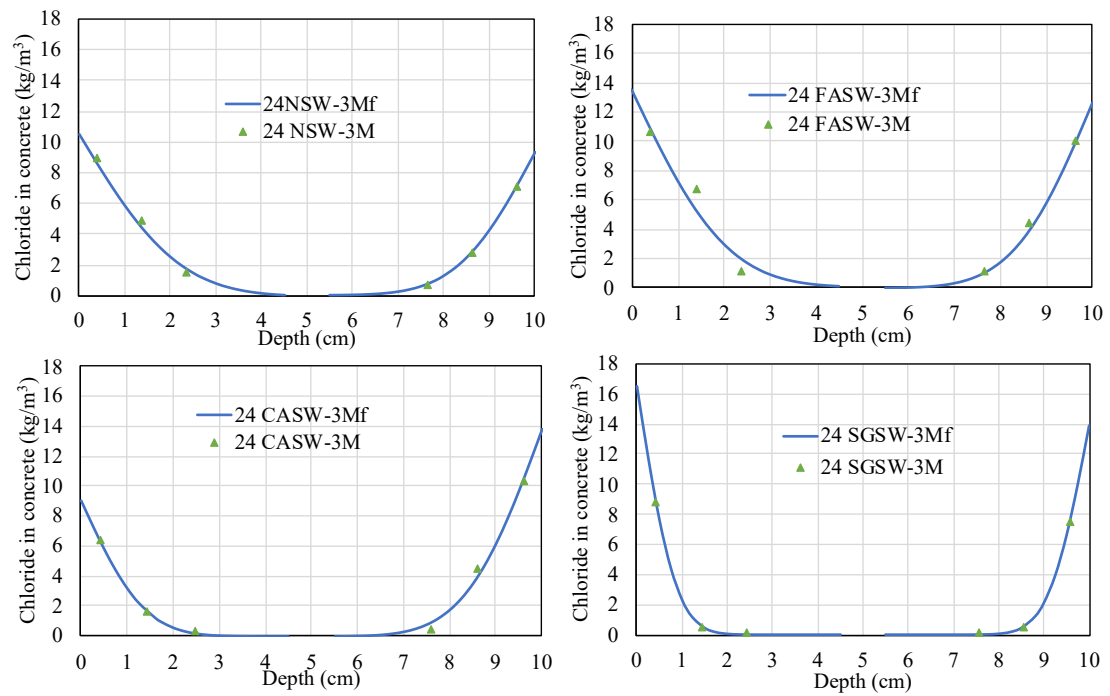


(b) Fitting curves of the 24S series at six months

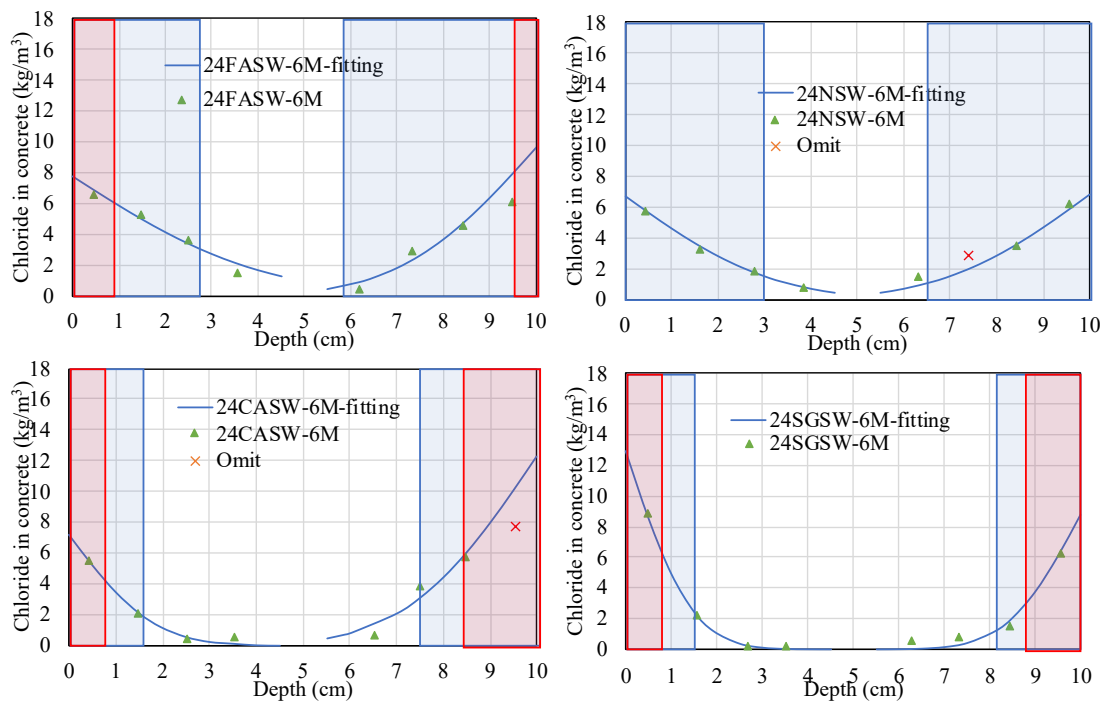


(c) Fitting curves of the 24S series at one year

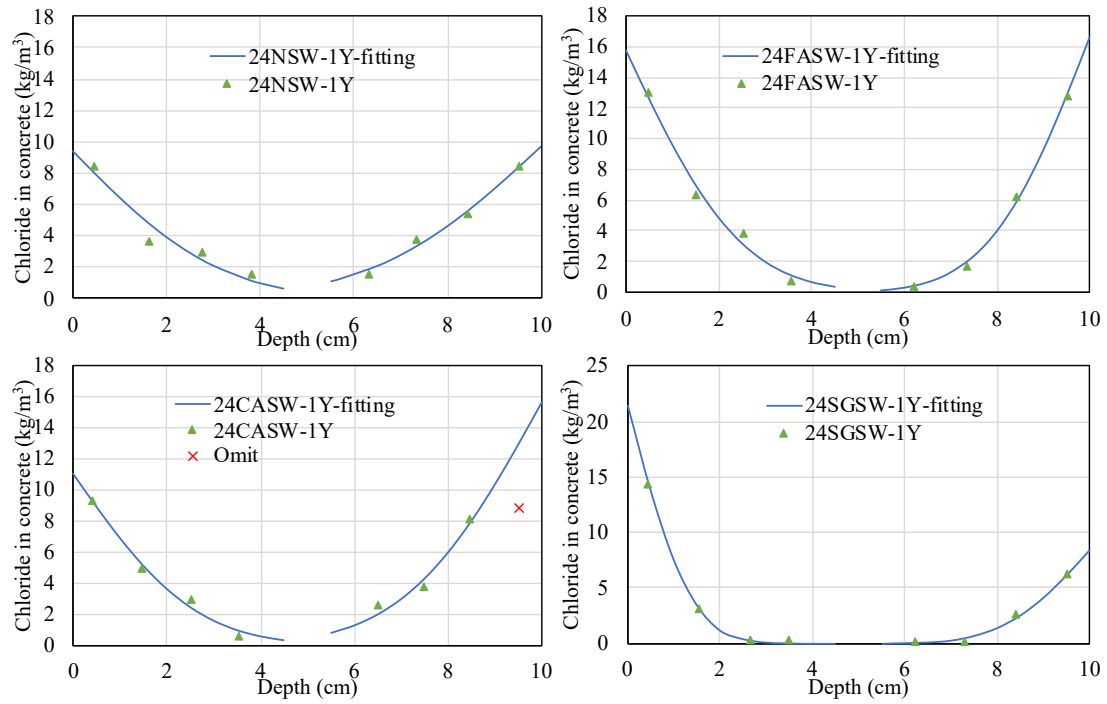
Appendix C (2) Fitting curves of the 24S series over one year



(a) Fitting curves of the 24SW series at three months

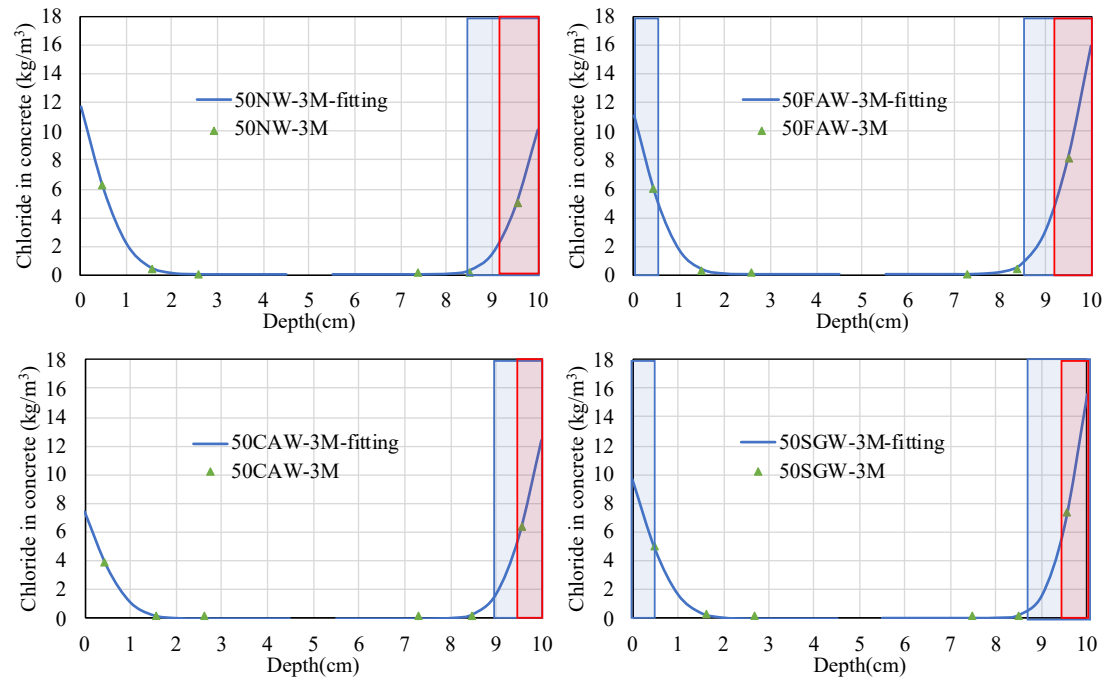


(b) Fitting curves of the 24SW series at six months

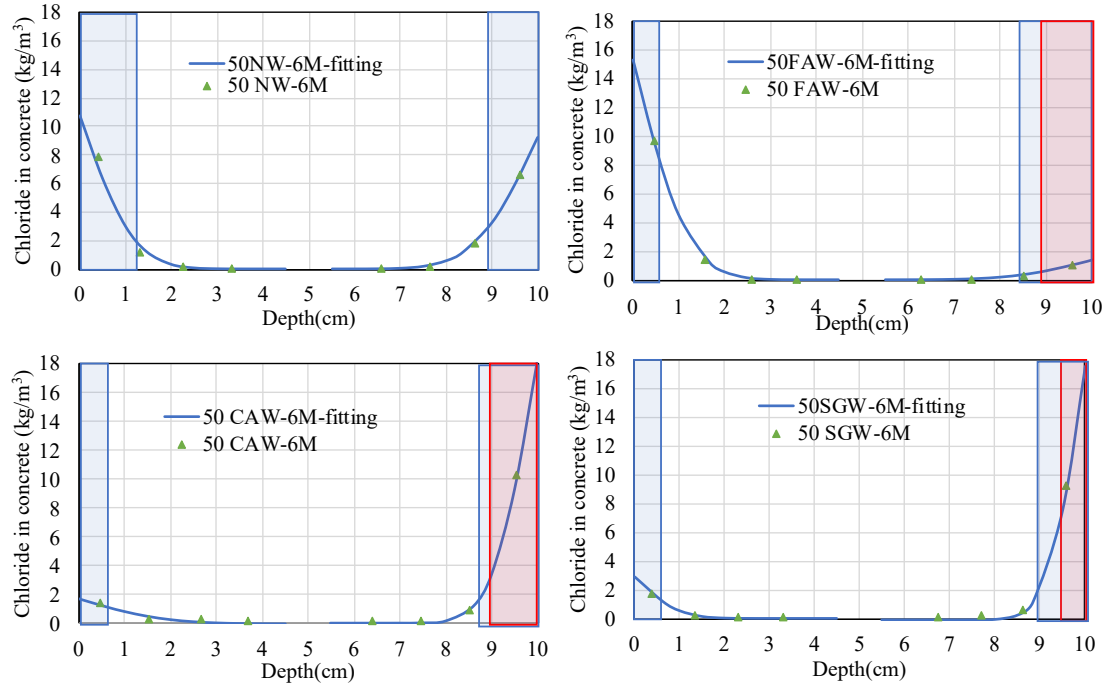


(c) Fitting curves of the 24SW series at one year

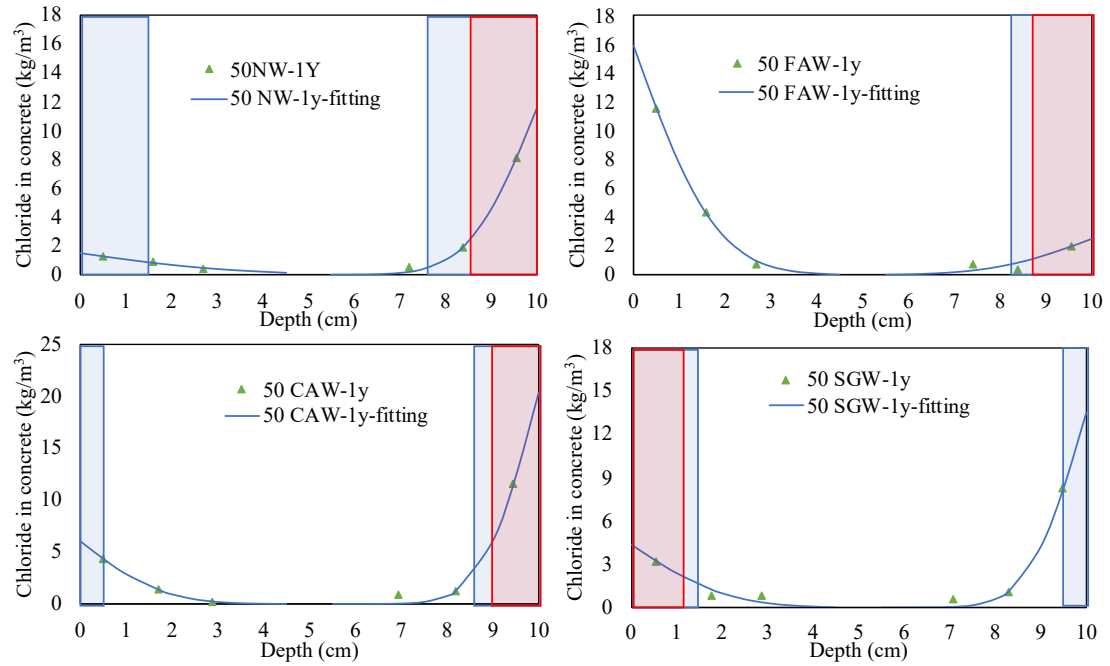
Appendix C (3) Fitting curves of the 24SW series over one year



(a) Fitting curves of the 50W series at three months

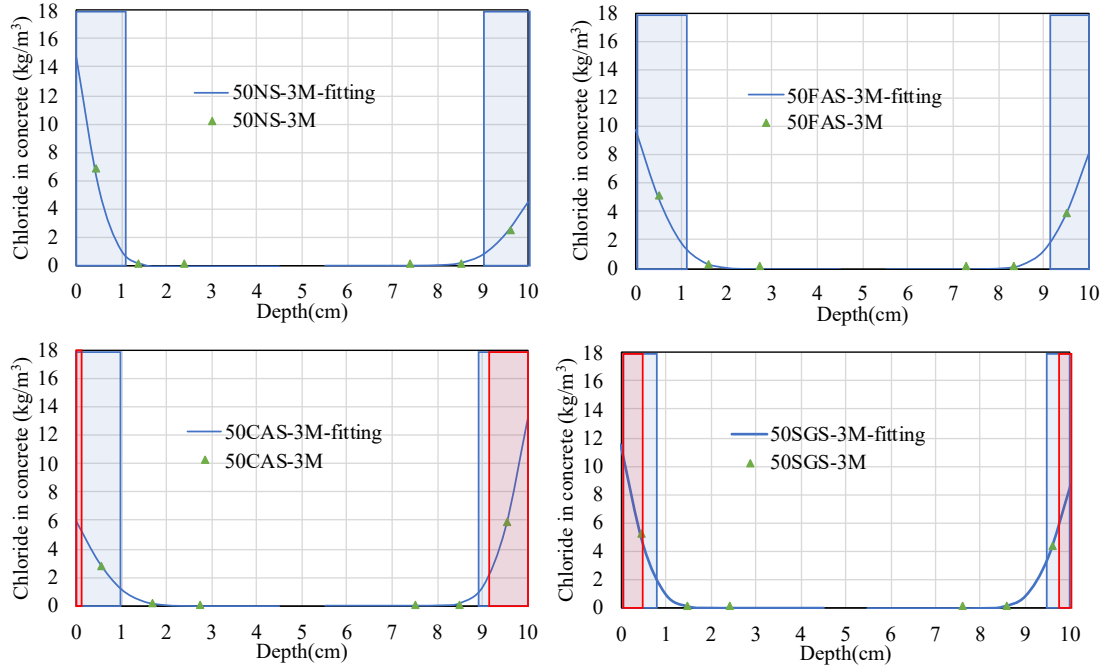


(b) Fitting curves of the 50W series at six months

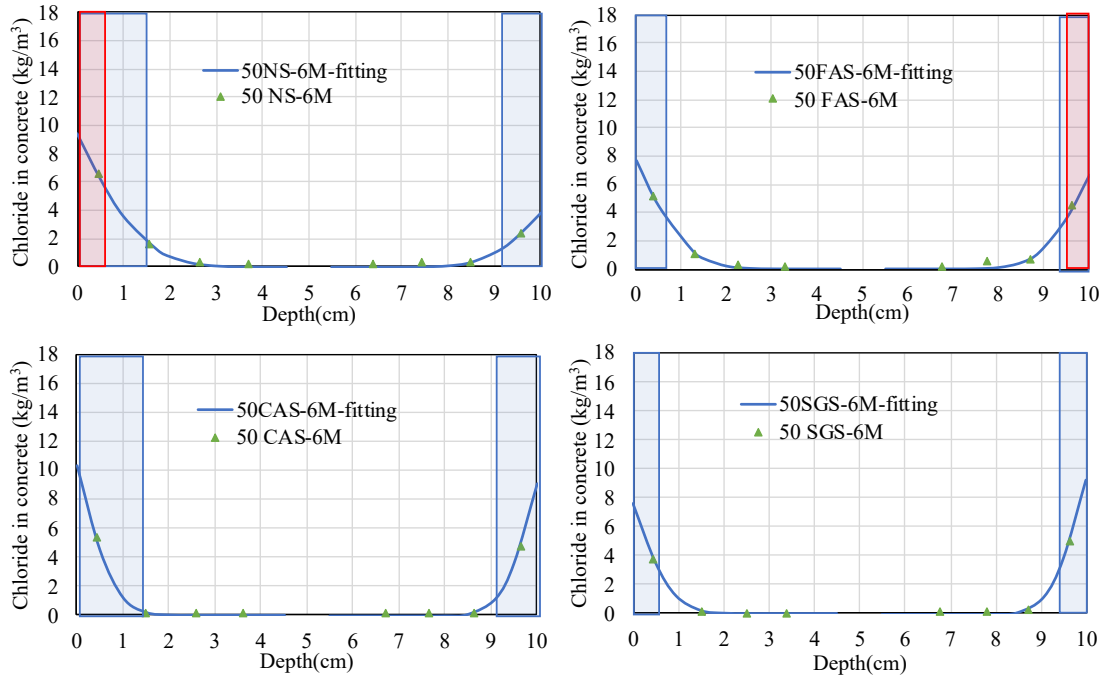


(c) Fitting curves of the 50W series at one year

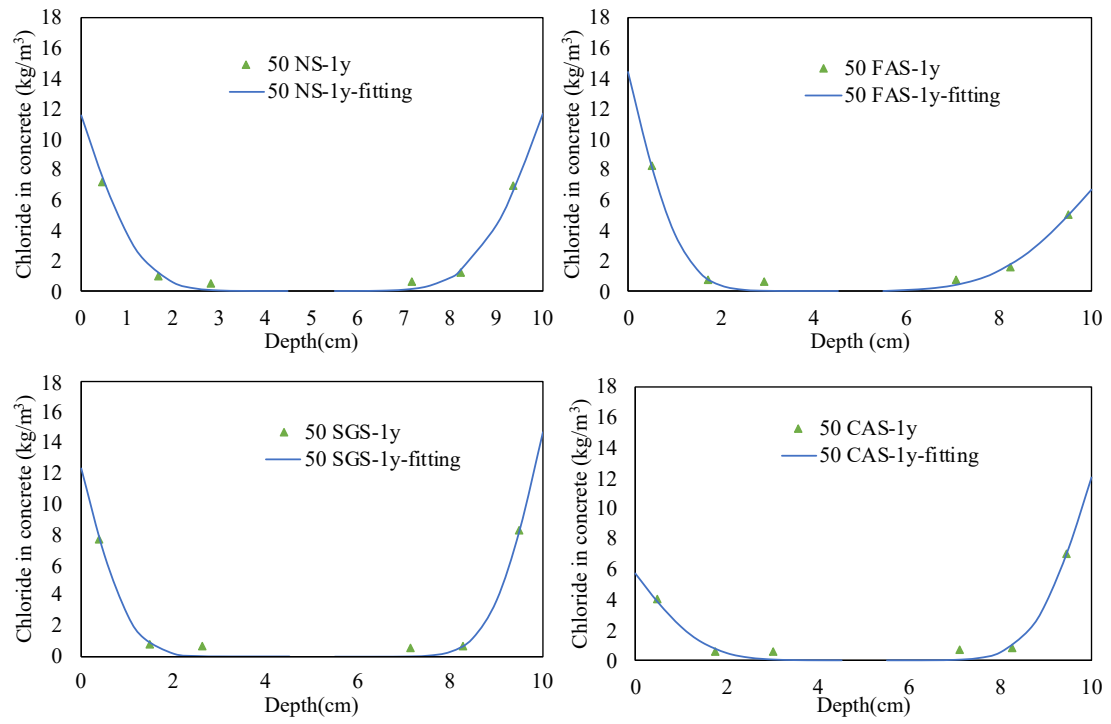
Appendix C (4) Fitting curves of the 50W series over one year



(a) Fitting curves of the 50S series at three months



(b) Fitting curves of the 50S series at six months



(c) Fitting curves of the 50S series at one year

Appendix C (5) Fitting curves of the 50S series over one year

APPENDIX D

1. Dc and C0 of 24W-3M, 24S-3M and 24SW-3M

24-3M	C0 (kg/m ³)	Dc (cm ² /year)	Ave (cm ² /year)
NWT-3M	2.63	2.30	2.55
NWB-3M	3.54	2.80	
NST-3M	7.38	9.84	7.86
NSB-3M	5.47	5.87	
NSTW-3M	10.5	5.86	4.73
NSWB-3M	9.31	3.60	
FAWT-3M	2.02	3.60	2.65
FAWB-3M	4.26	1.70	
FAST-3M	8.43	4.28	5.54
FASB-3M	7.38	6.80	
FASWT-3M	13.5	5.30	4.48
FASWB-3M	12.7	3.66	
CAWT-3M	5.50	1.12	1.33
CAWB-3M	10.3	1.53	
CAST-3M	8.66	1.13	1.16
CASB-3M	8.33	1.19	
CASWT-3M	9.01	2.33	2.90
CASWB-3M	13.8	3.48	
SGWT-3M	5.10	1.30	1.32
SGWB-3M	2.99	1.34	
SGST-3M	5.92	1.62	1.25
SGSB-3M	8.71	0.87	
SGSWT-3M	16.5	0.91	0.94
SGSWB-3M	13.9	0.97	

2. Dc and C0 of 24W-6M, 24S-6M and 24SW-6M

24-6M	C0 (kg/m ³)	Dc (cm ² /year)	Ave (cm ² /year)
NWT-6M	11.1	2.52	1.84
NWB-6M	12.8	1.16	
NST-6M	13.9	2.46	3.27
NSB-6M	11.1	4.09	
NSTW-6M	6.69	6.18	7.63
NSWB-6M	7.40	9.09	
FAWT-6M	6.13	2.36	1.67
FAWB-6M	6.50	0.99	
FAST-6M	9.35	3.37	3.35
FASB-6M	12.8	3.33	
FASWT-6M	7.73	10.0	8.75
FASWB-6M	7.44	7.44	
CAWT-6M	5.62	1.75	2.14
CAWB-6M	5.51	2.53	
CAST-6M	20.2	1.11	0.83
CASB-6M	24.3	0.54	
CASWT-6M	7.14	2.03	3.43
CASWB-6M	12.2	4.84	
SGWT-6M	13.9	0.78	0.59
SGWB-6M	6.36	0.41	
SGST-6M	15.5	1.87	1.18
SGSB-6M	16.1	0.50	
SGSWT-6M	13.0	1.30	1.45
SGSWB-6M	8.77	1.59	

3. Dc and C0 of 24W-1Y, 24S-1Y and 24SW-1Y

24-1Y	C0 (kg/m ³)	Dc (cm ² /year)	Ave (cm ² /year)
NWT-1Y	6.73	1.86	2.11
NWB-1Y	11.6	2.36	
NST-1Y	13.6	1.44	
NSB-1Y	11.1	2.68	2.06
NSWT-1Y	9.39	3.04	
NSWB-1Y	9.72	3.91	
FAWT-1Y	6.02	0.82	0.91
FAWB-1Y	12.6	1.01	
FAST-1Y	9.57	3.17	
FASB-1Y	11.2	2.85	3.01
FASWT-1Y	15.7	1.91	
FASWB-1Y	16.6	1.45	
CAWT-1Y	7.58	0.46	0.96
CAWB-1Y	14.1	1.46	
CAST-1Y	14.8	1.33	
CASB-1Y	26.4	0.83	1.08
CASWT-1Y	11.1	2.09	
CASWB-1Y	15.7	2.61	
SGWT-1Y	16.4	0.47	0.47
SGWB-1Y	9.57	0.46	
SGST-1Y	24.0	0.86	
SGSB-1Y	14.5	0.39	0.63
SGSWT-1Y	21.5	0.58	
SGSWB-1Y	8.36	1.07	

4. Dc ratio of 24SCM/24N series from three months to one year of seawater exposure

Dc ratio of 24SCM/24N series									
	W			S			SW		
	3M	6M	1Y	3M	6M	1Y	3M	6M	1Y
24FA/24N	0.79	1.04	0.43	0.71	1.02	1.46	0.95	1.15	0.48
24SG/24N	0.52	0.32	0.22	0.16	0.36	0.30	0.20	0.19	0.24
24CA/24N	0.52	1.16	0.45	0.15	0.25	0.53	0.61	0.45	0.68

5. Dc and C0 of 50W and 50S at three months

50-3M	C0 (kg/m ³)	Dc (cm ² /year)	Ave (cm ² /year)
NWT-3M	11.7	1.12	1.03
NWB-3M	10.08	0.93	
NST-3M	14.6	0.63	0.86
NSB-3M	4.44	1.09	
FAWT-3M	11.1	0.96	1.06
FAWB-3M	15.9	1.16	
FAST-3M	9.77	1.17	1.09
FASB-3M	8.09	1.01	
CAWT-3M	7.48	0.98	0.89
CAWB-3M	12.4	0.81	
CAST-3M	5.93	1.21	0.98
CASB-3M	13.3	0.75	
SGWT-3M	9.69	1.08	0.91
SGWB-3M	15.6	0.74	
SGST-3M	11.5	0.67	0.71
SGSB-3M	8.67	0.74	

6. Dc and C0 of 50W and 50S at six months

50-6M	C0 (kg/m ³)	Dc (cm ² /year)	Ave (cm ² /year)
NWT-6M	10.7	0.85	1.00
NWB-6M	9.27	1.16	
NST-6M	9.46	1.29	1.03
NSB-6M	3.82	0.77	
FAWT-6M	15.2	0.91	1.34
FAWB-6M	1.47	1.77	
FAST-6M	7.64	0.79	0.73
FASB-6M	6.69	0.68	
CAWT-6M	1.78	2.11	1.34
CAWB-6M	18.4	0.57	
CAST-6M	10.4	0.41	0.38
CASB-6M	9.04	0.36	
SGWT-6M	2.98	0.57	0.49
SGWB-6M	17.6	0.41	
SGST-6M	7.56	0.46	0.42
SGSB-6M	9.18	0.37	

7. Dc and C0 of 50W and 50S at one year

50-1Y	C0 (kg/m ³)	Dc (cm ² /year)	Ave (cm ² /year)
NWT-1Y	1.45	3.45*	0.68
NWB-1Y	11.5	0.68	
NST-1Y	11.5	0.52	
NSB-1Y	11.7	0.63	0.57
FAWT-1Y	15.9	1.02	1.02
FAWB-1Y	1.36	2.32*	
FAST-1Y	14.4	0.40	
FASB-1Y	2.45	1.22	0.81
CAWT-1Y	5.97	0.99	0.73
CAWB-1Y	20.4	0.46	
CAST-1Y	5.76	0.66	
CASB-1Y	12.1	0.49	0.58
SGWT-1Y	5.09	0.49	0.49
SGWB-1Y	13.6	0.49	
SGST-1Y	12.4	0.33	
SGSB-1Y	14.7	0.38	0.36

* Dc values had been omitted

APPENDIX E

1. Depths of the high chloride concentration region and the chloride diffusion front of 24 series (cm)

Depths of the high chloride concentration region and the chloride diffusion front (cm)												
	24W				24S				24SW			
	N	FA	SG	CA	N	FA	SG	CA	N	FA	SG	CA
T	3Mh	1.4	0.5	-	-	1.1	1.8	1.3	1.1			
	3Mf	2.6	1.7	0.7	0.5	2.3	3.3	1.9	1.3			
	3M*	1.3	1.3	0.7	0.5	1.2	1.5	0.6	0.2			
	6Mh	0.7	-	1.2	0.9	1.4	1.5	1.6	1.6	-	0.9	0.8
	6Mf	2.5	1.4	2.2	5.0	2.9	3.5	2.8	2.1	3.0	2.8	1.5
	6M*	1.8	1.4	1.0	-	1.5	2.0	1.2	0.5	3.0	1.9	0.7
	1Yh	-	-	1.4	-	2.1	1.5	1.4	1.7			
	1Yf	2.3	1.7	1.7	0.4	3.8	3.2	2.1	2.2			
	1YM*	2.3	1.7	0.4	0.4	1.7	1.7	0.7	0.5			
	3Mh	1.2	1.4	0.9	1.1	1.4	1.9	1.2	1.3			
B	3Mf	5.0	2.5	1.6	5.0	2.8	3.0	1.6	1.8			
	3M*	3.8	1.1	0.7	-	1.3	1.1	0.4	0.5			
	6Mh	1.1	0.5	1.2	1.4	1.4	1.8	1.1	1.3	-	0.5	1.2
	6Mf	2.7	2.4	1.8	1.9	2.9	5.0	1.7	1.8	3.4	4.2	1.9
	6M*	1.6	1.8	0.6	0.5	1.5	3.2	0.6	0.5	3.4	3.6	0.7
	1Yh	0.7	0.7	1.1	2.2	2.2	2.6	1.4	1.8			
	1Yf	3.6	2.0	1.6	3.1	3.8	3.9	1.9	2.3			
	1YM*	2.9	1.3	0.5	0.9	1.7	1.3	0.5	0.5			

2. Depths of the high chloride concentration region and the chloride diffusion front of 50 series (cm)

Depth of the high chloride concentration region and the chloride diffusion front (cm)									
		50W				50S			
		N	FA	SG	CA	N	FA	SG	CA
T	3Mh	-	-	-	-	-	0.1	0.5	-
	3Mo	-	0.5	0.5	-	1.1	1	0.8	1.1
	3M*	-	-	-	-	-	0.9	0.4	-
	6h	-	-	-	-	0.5	-	-	-
	6Mo	1.2	0.6	0.5	0.5	1.3	1.3	0.7	0.5
	6M*	-	-	-	-	0.7	-	-	-
	12Mh	-	-	1	-				
	12Mo	1.4	-	1.4	0.5				
	1Y*	-	-	0.4	-				
B	3Mh	0.9	0.9	0.7	0.6	-	0.9	0.3	-
	3Mo	1.6	1.5	1.3	1	1	1.1	0.6	0.9
	3M*	0.7	0.5	0.5	0.4	-	0.2	0.4	-
	6Mh	-	1	0.6	0.9	-	-	-	0.5
	6Mo	1.1	1.7	1	1.1	0.9	0.9	0.4	0.6
	6M*	-	0.7	0.4	0.2	-	-	-	0.2
	1Yh	1.5	1.3	-	1.1				
	1Yo	2.4	1.8	0.6	1.5				
	1Y*	0.9	0.5	-	0.4				

Depths are denoted with suffixes "h" and "f," respectively, while the "*" represents the distance from the boundary of the high-concentration region to the part free of chloride (unit: cm)

APPENDIX F

Corrosion current (Icorr) and Resistivity (Res) measured via Corrosion meter

	No.	Interval (days)	Icorr ($\mu\text{A}/\text{cm}^2$)		Icorr UT/JB	Resistivity ($\text{k}\Omega$)		Res UT/JB
			UT	JB		UT	JB	
FB	1	316	0.0	0.0	-	7.7	13.3	0.58
	2		0.0	0.0		7.2	15.7	0.46
	3		0.0	0.0		9.0	12.5	0.71
	4		0.0	0.0		9.0	13.2	0.68
	5		0.0	0.0		8.5	11.3	0.75
BB	1	590	0.004	0.004	0.84	6.64	7.16	0.93
	2		0.004	0.004	1.03	8.02	7.37	1.09
	3		0.006	0.004	1.46	7.81	8.31	0.94
	4		0.004	0.004	1.04	7.38	8.83	0.84
	5		0.27	0.014	19.86	7.38	8.83	0.84